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Conjugated Substituted Ionic Polyacetylenes

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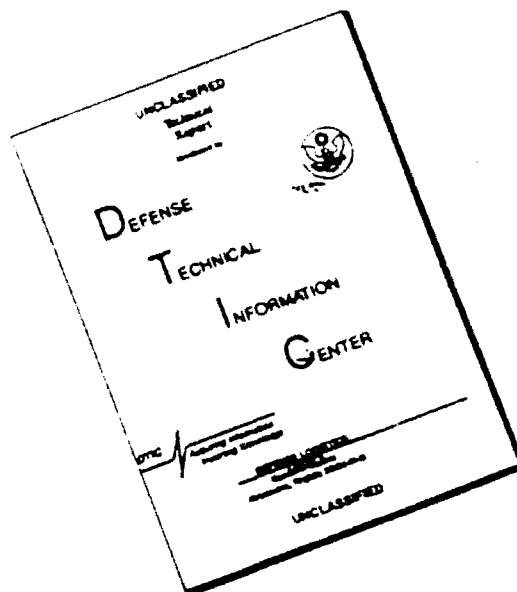
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Technical Report No. 1

**Conjugated Ionic Polyacetylenes 6. Polymerization of
2-Ethynylpyridinium Triflates**

by

Sundar Subramayam, M.S. Chetan and Alexandre Blumstein

Prepared for Publication

in

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Lowell, Massachusetts

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CONJUGATED IONIC POLYACETYLENES 6. POLYMERIZATION OF 2-ETHYNYLPYRIDINIUM TRIFLATES¹⁻⁶

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Abstract

A new method for polymerization of the acetylenic bond in 2-ethynylpyridine and its trimethylsilyl derivative is described. The acetylenic triple bond is activated by quaternization of the pyridine nitrogen by methyltrifluoromethanesulfonate (triflate). The resulting N-methylethynylpyridinium triflate salts polymerize readily to the corresponding poly[N-methylethynylpyridinium acetylene]triflates when treated with a nucleophilic initiator such as pyridine, or with a free radical initiator (AIBN). The product polymers are substituted ionic polyacetylenes of low DP with extensive backbone conjugation. Spectral data indicate that the conjugation in these systems is, by far, the highest observed for substituted polyacetylenes.

Introduction

The introduction of substituents on backbone carbons of *trans*-polyacetylene offers advantages of improved processability and greater oxidative stability compared to the unsubstituted state. It results, however, in substantial lowering of electrical conductivity and of the third order non-linear optical susceptibility, χ_3 . This is mainly attributed to the loss of conjugation that

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IR (cm^{-1}) 3251 ($\equiv\text{C-H}$ stretching), 2121 ($\text{C}\equiv\text{C}$ stretching), 1260 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV, (CH_3CN) λ_{max} C=C (nm) 260; Anal. (Calc. %) C = 40.45, H = 3.00, N = 5.24, S = 11.98; (Found %) C = 40.29, H = 2.90, N = 5.15, S = 12.14.

2-(trimethylsilyl-N-methylethynyl)pyridiniumtriflate 9: Was prepared in an identical manner using 1.3g (6.84×10^{-3} mol.) of 2-(trimethylsilylethynyl)pyridine and 1.0g, (5.7×10^{-3} mol.) of methyltrifluoromethanesulfonate. The crude product was obtained as a white solid that was recrystallized from toluene (1.8g). It was readily soluble in polar solvents; mp 81°C (DSC).

IR (cm^{-1}) 2119 ($\text{C}\equiv\text{C}$ stretching), 1274 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV, (CH_3CN) λ_{max} C=C (nm) 256; Anal. (Calc. %) C = 42.48, H = 4.72, N = 4.13, S = 9.44; (Found %) C = 42.21, H = 4.72, N = 4.07, S = 9.48.

Poly(N-methyl-2-ethynylpyridiniumacetylene)triflate 8p: Polymerization was carried out by three methods: (α) initiation with 1-2 mol % of pyridine in CH_3CN or in DMSO at 20°C for 24 hrs and (β) initiation with 0.5 mol % of 2,2'-azobis-(isobutyronitrile) (AIBN) at 70°C for 15 hrs and (γ) thermally by heating at 170°C for 1hr. in a sealed ampoule under argon atmosphere (Note: The monomer salt polymerizes when heated in air to its melting point). The product polymers were purified by removal of solvent followed by extraction with ether. They were then dissolved in acetonitrile and reprecipitated in ether. All samples were dried in vacuum at 40°C for 24 hrs. The polymer structures were confirmed by spectral methods and elemental composition.

8p α : IR cm⁻¹ 1613 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV, λ_{max} C=C (nm), 598 ; η_{inh} , (dL/g) 0.25.

Anal. (Calc. %) C = 40.45, H = 3.00, N = 5.24; (Found %) C = 42.55; H = 3.90; N = 6.19.

8p β : IR cm⁻¹ 1620 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1029 (S=O symmetric stretch); UV (CH₃CN), λ_{max} C=C (nm), 384, 908 (710 in H₂O) ; η_{inh} , (DMSO), 0.05 dL/g. Anal. (Calc. %) C = 40.45, H = 3.00, N = 5.24, S = 11.98; (Found %) C = 39.04; H = 3.13; N = 5.12; S = 11.98.

8p γ : IR cm⁻¹ 1622 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1029 (S=O symmetric stretch); UV (CH₃CN), continuous band trailing to 900 nm; η_{inh} , (CH₃CN), 0.05 dL/g.

Poly(2-trimethylsilyl-N-methylethynyl)pyridiniumacetylene)triflate 9p :

Was prepared in a similar manner using method (α). The polymer was isolated as a black lustrous solid that was soluble in chloroform but insoluble in ether.

IR (method a) cm⁻¹ 1620 (backbone C=C stretch), ; UV, (CH₃CN) λ_{max} C=C (nm), 574 (shoulder), 610 ; η_{inh} , (CH₃CN), 0.2 dL/g; Anal. (Calc. %) C = 42.48, H = 4.72, N = 4.13; (Found %) C = 43.53; H = 3.59; N = 6.63.

Results and Discussion:

Thermal properties

Monomer triflate salts **8** and **9** are crystalline solids that are thermally stable at room temperature in the solid state and as solutions in non nucleophilic solvents. The DSC thermogram of **8** shows two endotherms at 100°C and 155°C upon heating that arise from a crystal-crystal and a crystal - isotropic transition respectively. This is immediately followed by a broad exotherm likely resulting from thermal polymerization in the melt (Figure 2).

The crystal-crystal transition at 100°C is completely reversible through successive heating and cooling scans below the crystal melting temperature. The TGA thermogram of monomer **8** shows no weight loss until 360°C [Fig.2 (inset)], which precludes the possibility of loss of hydrated water that might contribute towards this endothermic transition. Furthermore, it is evident that the large exotherm is not due to a degradative decomposition of the monomer, since no weight loss is detected at this temperature. This is confirmed by the thermal behavior of polymers **8p** α , β and γ , all of which show a major weight loss starting at 360°C. The thermal stability of these polyethynylpyridinium triflates is substantially higher than that of the corresponding iodides⁴. Their oxidative stability is similar to the iodides (TGA thermograms in air and in nitrogen are identical with respect to the degradation temperature for respective polymers). The thermal behavior of the ethynylpyridinium triflate monomers is similar to the corresponding 4-N-alkylvinylpyridinium triflates which also undergo spontaneous polymerization upon melting to give polyvinyl-4-N-alkylpyridiniumtriflates.^{10,11}

Melt polymerization in an inert atmosphere of monomer **8** resulted in a black, polymeric product which is indicative of a conjugated polyene backbone. Its infrared spectrum shows a band at 1622 cm⁻¹ (C=C stretch), while the acetylenic bands of the starting monomer are absent. The UV-visible spectrum exhibits a continuous absorption band trailing to 900 nm in the near infrared region. This is perhaps indicative of a wide distribution of conjugated polyene segments with low molar masses ($\eta_{inh} = 0.05$ dL/g).

The thermal behavior of monomer salt **9** is markedly different from that of **8**. Figure 3 shows the DSC thermogram for the monomer, which shows a possible crystal-crystal transition at 70°C that is immediately followed by crystalline melting. The crystal-isotropic transition occurs at a much lower

temperature (ca 81°C), and results in a stable isotropic melt. No thermal polymerization was observed until its decomposition temperature (150°C) as is evidenced from the TGA thermogram of the monomer [Fig. 3 (inset)]. The relatively lower crystalline melting temperature and the poor thermal reactivity for **9** can both be attributed to steric factors introduced by the bulky trimethylsilyl substituent, which is also responsible for its lower decomposition temperature. Table 1 lists the crystal-crystal transition, melting and decomposition temperatures together with corresponding enthalpies for monomers **3** and **9**.

The thermal reactivity of the acetylenic triple bond in **8** is not surprising. It is well known that activation of the carbon-carbon triple bond by introduction of strongly electron withdrawing groups on the acetylenic carbons enhances their reactivity. The increased reactivity of the acetylenic bond in the quaternized ethynylpyridines is attributed to the strongly electron-withdrawing nature of the pyridinium substituents, which effectively lower the energy of the Lowest Unoccupied Molecular Orbital (LUMO) of the acetylenic moiety.¹² A Diels-Alder reaction involving ethynylpyridinium salts was first reported by Yamashita and coworkers^{12,13}, who observed that 1,2-bis-2-pyridyl and 4-pyridylethynylpyridinium salts showed substantially enhanced dienophilic character and readily underwent cycloaddition with cyclopentadiene. The corresponding unquaternized bis-pyridylethyne, however, do not undergo cycloaddition even under drastic conditions. The reactivity of the acetylenic moiety is also greatly dependent on the position of the nitrogen atom in the pyridinium group with respect to the triple bond. The acetylenic bond in 1,2-bis-2-pyridiniumethyne, for example, was found to be most reactive in Diels Alder reactions, followed by the corresponding 4-pyridinium derivative. The 3-pyridinium salt in contrast, showed poor reactivity even under severe conditions since the pyridinium nitrogen is not in conjugation with the acetylenic triple bond.¹³ From the present

study, it is evident that such activated triple bonds are also susceptible to a free radical attack.

Polymerization initiated by nucleophiles

The monomer triflate salts **8** and **9** polymerize readily in polar solvents such as CH₃CN and DMSO in the presence of a nucleophilic initiator such as pyridine. The product polymers **8pα** and **9pα** are black, lustrous solids that are hygroscopic and soluble in polar solvents and in water. Their infrared spectra indicate the absence of the absorption bands due to the acetylenic group that occur at 3251 and 2121 cm⁻¹ (≡C-H and C≡C stretch) for **8** and 2119 cm⁻¹ (C≡C stretch) for **9**. They are replaced by a strong bands at 1613 and 1620 cm⁻¹ respectively which arise from the backbone C=C stretch. Figure 4 shows the IR spectra for monomer **8** and polymer **8pα**. The UV-VIS spectra for polymers **8pα** and **9pα** show strong absorption bands at 598 and 610 nm respectively compared to the corresponding monomer salts that do not absorb beyond 330 nm. This is indicative of their extensively conjugated structures. The similarity in the absorption maxima for **8pα** and **9pα** is surprising in view of the bulky trimethylsilyl (TMS) substituents in the latter. Modeling studies performed by us on such systems using dynamic mechanical simulation methods have shown that both the *trans-transoidal* and *cis-transoidal* conformations are energetically favored.⁷ Both conformers give rise to a conjugated polyene backbone due to strong electrostatic interactions between the side group pyridinium rings and the counterions. This is supported by the fact that monomers **8** and **9** when polymerized by molecular bromine resulted in conjugated polyenes of which only the polymer derived from **8** displayed excimer fluorescence.⁵ Stacking of pyridinium rings along the backbone is possible only in a *trans-transoidal* conformation. This suggests that a *trans-transoidal* conformation is probably favored in the former and *cis-transoidal*

one in the latter, thus obviating the steric factors that are associated with the bulky TMS groups.

The present polymerization reactions presumably occur via a nucleophilic attack by pyridine on the acetylenic carbon of the monomer salt. It is proposed that the reaction proceeds via an initiation step that involves the formation of a macrozwitterion (Scheme 1). The addition of tertiary amines such as pyridine to activated acetylenes is known to proceed via a bimolecular nucleophilic addition that results in the formation of a zwitterion.¹⁴ Although this intermediate ion has not been isolated for amine initiated reactions, the vinyl anion that is formed has been isolated and trapped in the reaction of acetylene-bis-methylcarboxylate upon initiation with triphenyl phosphine.¹⁵ Based on orbital considerations, it has been suggested that an open, stereo stable '*anti*' anion is formed, resulting in the *anti* course of the 1,2 addition.¹⁴ The non spontaneous, nucleophile initiated polymerization of these ethynylpyridinium triflate salts also tends to substantiate the activation and initiation steps proposed by us previously for the spontaneous polymerization of ethynylpyridines via a Menschutkin reaction.⁴ An initiation step involving a nucleophilic attack on the acetylenic carbon of the activated, quaternized monomer by unquaternized species was envisaged for those reactions. The exact nature of the reaction mechanism, however, remains unclear at present. A detailed kinetic study is ongoing and will be the subject of a separate paper.

The molecular weights of the present polymers did not, however, increase substantially ($\eta_{inh} = 0.2-0.25$ dL/g) in spite of eliminating the possibility of termination by excess quaternizing agent that posed a problem in the spontaneous polymerizations. This implies that an alternative rapid termination process is operative here. A possible explanation could lie in the macrozwitterionic nature of the propagating species proposed in Scheme 1.

Polymerization of vinyl monomers initiated by neutral nucleophilic initiators have been known to result in low degrees of polymerization (D_p).¹⁴ This is generally attributed to two factors (i) substantially reduced nucleophilicity of the zwitterionic species generated upon initiation and due to the proximity of opposite charges; the subsequent propagation step is, therefore, slow and (ii) lack of stabilization for the carbanion in the growing polyene chain possibly resulting in a rapid termination. Stabilization of the carbanion in the growing polymer chain has been found to be an important factor that leads to increase in molecular weight for polymerizations via zwitterionic propagation.¹⁴ In the case of highly stabilized carbanions, the polymerization acquires a living character at very low temperatures.¹⁶⁻¹⁸ Our modeling studies reveal that the side group pyridinium rings are nearly orthogonal to the polyene backbone.⁷ This suggests that the intermediate carbanion is not greatly stabilized by the pyridinium substituents thereby resulting in low molar masses. The possibility of termination by chain transfer to monomer is, therefore, an additional factor that could have an adverse effect on the D_p in these reactions.

The formation of cyclic side products during polymerization of the monomer triflate salts **8** and **9** was also examined. In a recent paper, Fife et al⁹ reported that in the reaction of 1-methyl-4-ethynylpyridiniumtriflate in aqueous DMSO upon heating to 100°C for 2 hours, cyclotrimerization of the monomer salt occurred to form 1,3,5-tris(1-methyl-4-pyridino)benzene triflate in addition to a polymeric product. The corresponding N-protonated triflate, however, did not result in a cyclic compound.⁹ Attempts to isolate such cyclic trimerization products by precipitation methods used in the above study were unsuccessful for monomer salts **8** and **9** polymerized under the reaction conditions outlined in the present study. We believe that the formation of cyclic products to be highly unlikely in the present case due to the following (i) the steric factors

involved with the alkyl substituent on the pyridinium nitrogen in the 2- position, especially in the case of monomer 9, wherein the formation of a cyclic trimer would be severely hindered by the bulky trimethylsilyl group (ii) substantially lower reaction temperatures (reactions were run at 0° and 20° C) in non aqueous solvents; both 2- and 4-ethynylpyridinium triflate salts are stable in solutions of water and DMSO at these temperatures and (iii) low concentration of the nucleophilic initiator (1-2 mol %).

The conjugation lengths based on spectral data for the ionic polyacetylenes obtained by the presently described non spontaneous method is greater compared to those obtained by methods involving spontaneous processes⁴⁻⁶ and is, by far, the highest reported for substituted polyacetylenes. Table 2 lists the spectral data and the calculated conjugation number n for ionic polyacetylenes synthesized by different methods. Contribution to λ_{\max} from the charged pyridinium chromophores is unlikely, since no substantial shift is observed in the absorption maxima of poly-4-vinylpyridiniumbromide compared to the corresponding uncharged poly-4-vinylpyridine (260 and 250 nm respectively).¹⁹

We have previously determined that the conjugation number (n) obtained from the absorption maxima for such ionic polyenes (using the Lewis Calvin equation^{20,21}) may be correlated to their degree of polymerization (D_p), assuming fully conjugated backbone. This was substantiated by comparing the calculated D_p with the experimental one determined from M_n measured by vapor pressure osmometry.⁶ It was found that n can be related to D_p (within the experimental error of 20%) for up to $n = 16$.⁶ Based on these results polymers 8p α and 9p α should have D_p values of ≥ 16 . It must be emphasized however, that the calculated values of n are only an approximate, since the relation $\lambda^2 = kn$ becomes increasingly nonlinear and saturates at about 30 for

conjugated polyenes.²² Based on a band gap energy of 2.4 eV for fully *trans*-polyacetylene, the λ_{max} (C=C) saturates at ~630 nm.²² Hence the C=C absorption maximum is no longer sensitive to the conjugation number of the polyene chain.

Polymerization with free radical initiator

Polymerization of monomer salt **8** with azobisisobutyronitrile (AIBN) in acetonitrile resulted in a black solid (**8p β**) whose infrared spectrum resembled those of the ionic polyacetylenes obtained by using a nucleophile initiator. The acetylenic $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ bands of the monomer are replaced by a strong band at 1620 cm^{-1} from the backbone C=C stretch. The molecular weight of the resulting polymer is very low ($\eta_{\text{inh}} = 0.05\text{ dL/g}$) i.e. in the oligomeric range. This is also supported by the C=C absorption band at 384 nm which is in contrast to the corresponding polymer obtained by nucleophilic initiation that occurs at 598 nm. The UV/VIS/NIR spectrum of **8p β** , however, shows a long wavelength absorption band at 908 nm that was not displayed by corresponding polyenes obtained by other methods. Figure 5 shows the UV/VIS/NIR spectra of monomer **8** and polymers **8p α** , **8p β** and **8p γ** .

The low value of η_{inh} oligomer **8p β** is similar to those obtained by Gal et al²³ in the attempted polymerization of 2- and 4-ethynylpyridine using transition metal catalysts. This is in contrast to the polymerization of phenylacetylene by coordination catalysts which yield high molecular weight polyacetylenes.²⁴ An unfavorable chain transfer termination process that competes effectively with propagation might possibly account for the low molar masses for ethynyl pyridine and its derivatives.

Unlike **8**, monomer **9** did not undergo a polymerization reaction by free radical initiation; the starting monomer was recovered after reaction with AIBN

for 30 hours. Introduction of a trimethylsilyl group on the acetylenic carbon in 2-N-methylethynylpyridinium triflate drastically affects the susceptibility of the acetylenic bond to free radically initiated polymerization. This is also evidenced by the reluctance of **9** to undergo thermal polymerization upon melting. This is not surprising, since it is well known that free radical initiation of monomers containing 1,2 disubstituted multiple bonds is difficult.

The UV-VIS/NIR spectra of **8p β** show some remarkable solvent dependent properties that were not observed for the corresponding polyacetylenes obtained by other methods. The spectrum recorded immediately upon dissolution in acetonitrile showed an absorption band at 908 nm trailing to 1050nm (near IR) and another at 384nm. The longer wavelength band underwent a hypsochromic shift with time, reaching an equilibrium value at 854 nm. When the polymer was dissolved in water, a large hypsochromic shift of this band to 710nm occurs, together with a decrease in intensity of the shorter wavelength absorption. The color of the polymer solution changes from red-brown in acetonitrile to blue in water. Figure 6 shows the UV-VIS/NIR spectra of the polymer in the two solvents. Addition of water to an acetonitrile solution also produces the hypsochromic shift. The progressive shift in the absorption maximum of the long wavelength band as a function of time in an acetonitrile-water solution of fixed composition is shown in Figure 7. The spectra pass through an isobiestic point at 765 nm, which suggests that the conformational change giving rise to this solvatochromic shift is an equilibrium process. This is also supported by the fact that complete evaporation of solvent from an aqueous solution of the polymer followed by its redissolution in acetonitrile produces a bathochromic shift of the long wavelength band in the absorption spectrum, which resembles the one originally recorded in this solvent. Such solvatochromic behavior which is more commonly observed for soluble

polydiacetylenes and is attributed to backbone conformational changes in solution^{25,26}, is unusual for polyacetylenes due to their rigid backbones. The present example provides, what we believe, to be the first known example of solvatochromism in polyacetylenes. Additionally, both the wavelengths of the absorption maxima and the magnitude of the shift is substantially larger than those reported for polydiacetylenes.

The factors responsible for the solvatochromic effect in the present polyene are not completely understood in view of its rigid structural characteristics that does not allow for conformational changes in the backbone. A tentative explanation of this most interesting effect is that it may be due to the presence of structural defects in the polyene backbone that are introduced by free radical polymerization such as a more frequent "tail to tail" sequencing than in the corresponding polyene prepared by nucleophile initiation. Such defects would increase the distance between adjacent pyridinium rings, which would now require a near coplanar arrangement of the rings with respect to the backbone for efficient interaction with the triflate counterions. This is in contrast to the regular "head to tail" arrangement wherein the rings are close to orthogonal for such an interaction. Such a coplanar conformation would result in a substantial reduction in the band gap energy that in turn, would cause the absorption band in the electronic spectrum to shift to the near infrared region. Modeling studies by Orchard and Tripathy²⁷ on the effect of substituent conformation on the electronic properties of substituted polydiacetylenes using dynamic mechanical simulations is in support of this view. Their study showed that a coplanar conformation of an electron withdrawing substituent with the polyene backbone results in a substantial decrease in the band gap energy compared to a non coplanar arrangement. This is reflected by a large red shift in the absorption spectrum for the coplanar arrangement with respect to the

non coplanar one. The instantaneous spectrum of polymer 8p β in acetonitrile may be approximated to that in the solid state wherein pyridinium rings at defect sites are in a coplanar arrangement, with adjacent rings interacting with the triflate counterions. Solvation of the pyridinium groups (and of the counterions) at defect sites would considerably reduce this interaction, thus allowing for rotation to a non planar conformation. This would explain the progressive blue shift in the absorption spectrum with increasing solvation. The high degree of solvation in water compared to acetonitrile could account for the larger hypsochromic effect in an aqueous solution. This aspect is being currently investigated in detail and will be the subject of a separate paper.

Summary

The preparation of activated ethynylpyridinium monomers enables the separation of the quaternization (activation) step from their polymerization. The activated monomers can be polymerized in a controlled manner with appropriate initiators. The presently described non spontaneous method for polymerization of activated acetylenic monomers provides a relatively simple route for the synthesis of substituted ionic polyacetylenes with backbone conjugation lengths that are relatively higher than those obtained by spontaneous processes. These activated monomers also allow polymerization of the acetylenic triple bond via free radical initiation; the latter process, is most unusual, since the acetylenic bond is not very susceptible to free radical initiation. The oligomer obtained by radical initiation displays a most interesting solvatochromic effect which is uncommon for polyacetylenes. This could be of considerable interest especially in terms of its possible high third order non linear optical susceptibility (χ_3).

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References and Notes

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Figure 1. General structure of ionic polyacetylenes

Figure 2. DSC and TGA (inset) thermograms of N-methyl-2-ethynylpyridiniumtriflate (**8**) in nitrogen; heating rates 20° and 10°/min respectively.

Figure 3. DSC and TGA (inset) thermograms of 2-(trimethylsilyl-N-methyl-ethynyl)pyridiniumtriflate (**9**) in nitrogen; heating rates 2.5° and 10°/min respectively.

Figure 4. Infrared spectra of (a) monomer **8** and (b) polymer **8p α** .

Scheme 1. Overall reaction pathway for nucleophile initiated polymerization.

Figure 5. UV-VIS/NIR spectra of monomer **8** and polymers **8p** in CH₃CN at 22°C (conc.= 10⁻⁶ g/L).

Figure 6. UV-VIS/NIR spectra of polymer **8p β** (a) instantaneous spectrum in CH₃CN (b) after equilibration for 120 min. in CH₃CN (c) in H₂O (All concs.= 10⁻⁶ g/L).

Figure 7. Shift in absorption maximum of polymer **8p β** in CH₃CN after addition of 95% water at 22°C with time (a) 45 min. (b) 90 min. (c) 120 min. (d) 150 min (All concs.= 10⁻⁶ g/L).

Table 1. Transition temperatures (°C) and enthalpies of transition (J/g) for
2-ethynylpyridiniumtriflate salts

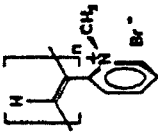
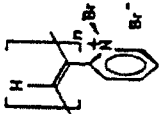
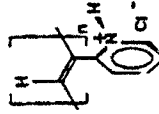
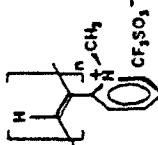
Monomer	T _{K-K}	ΔH _{K-K}	T _m	ΔH _m	T _p	ΔH _p	T _d [†]
8	100	49.9	157	33.2	170	-570	360
9	70	5.8	81	57.8	-	-	150

Transition temperatures and enthalpies measured by DSC

[†]Decomposition temperatures from TGA

K-K = crystal-crystal; m = melting; p = polymerization; d = decomposition

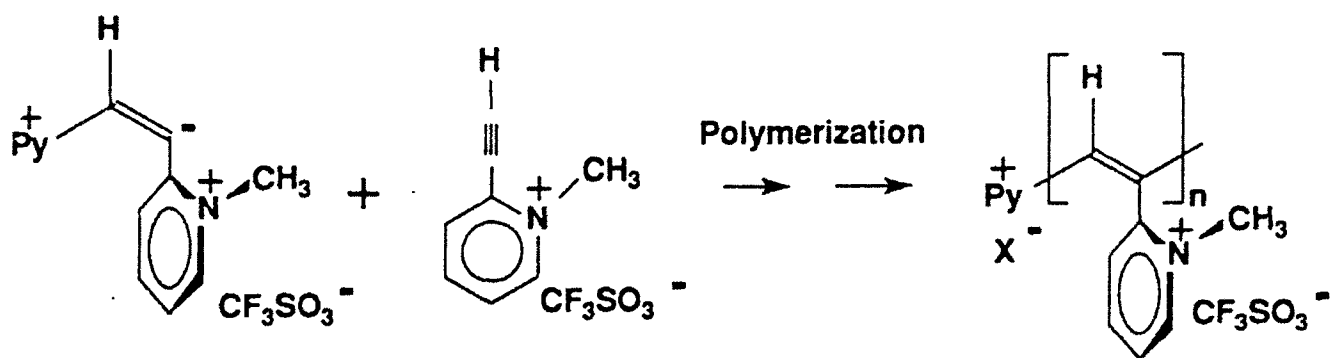
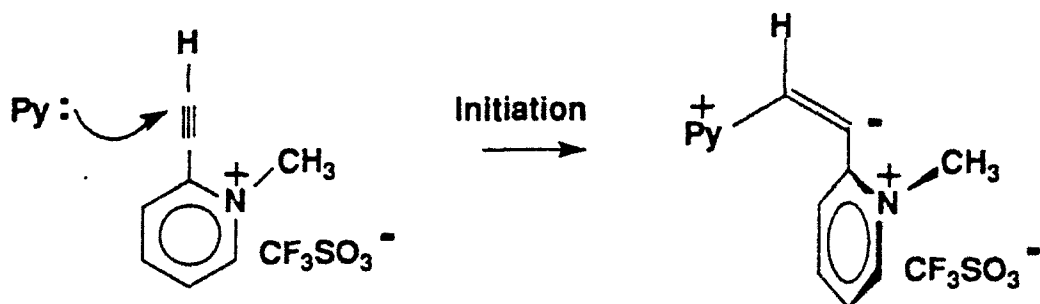
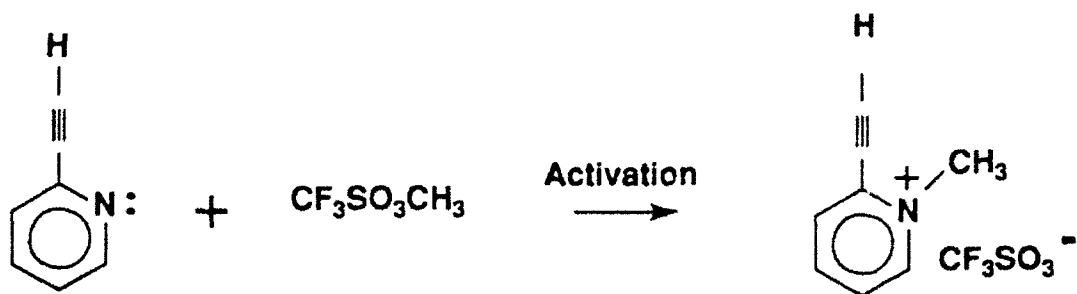
Table 2. Absorption maxima and conjugation lengths (n) of ionic polyacetylenes obtained by nucleophilic initiation

Method	Structure	λ_{\max} (C=C) ^a (nm)	n^b (calc.)	$(\eta)_{inh}^c$ dL/g	Ref.
Menschutkin reaction		370-480	8-12	0.1-0.2	3,4
Halogen complex		450	11	0.1	5
Protonation		530	15	0.2	6
Triflate salts		600	>16	0.2-0.25	this work

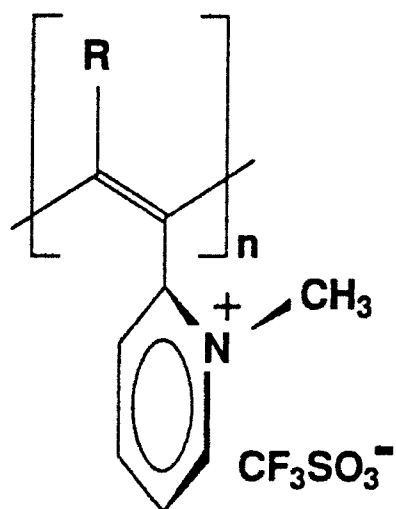
^a From UV-VIS. spectra

^b From Lewis Calvin equation (Ref. 20)

^c at 28°C, conc. = 0.5 g/dL

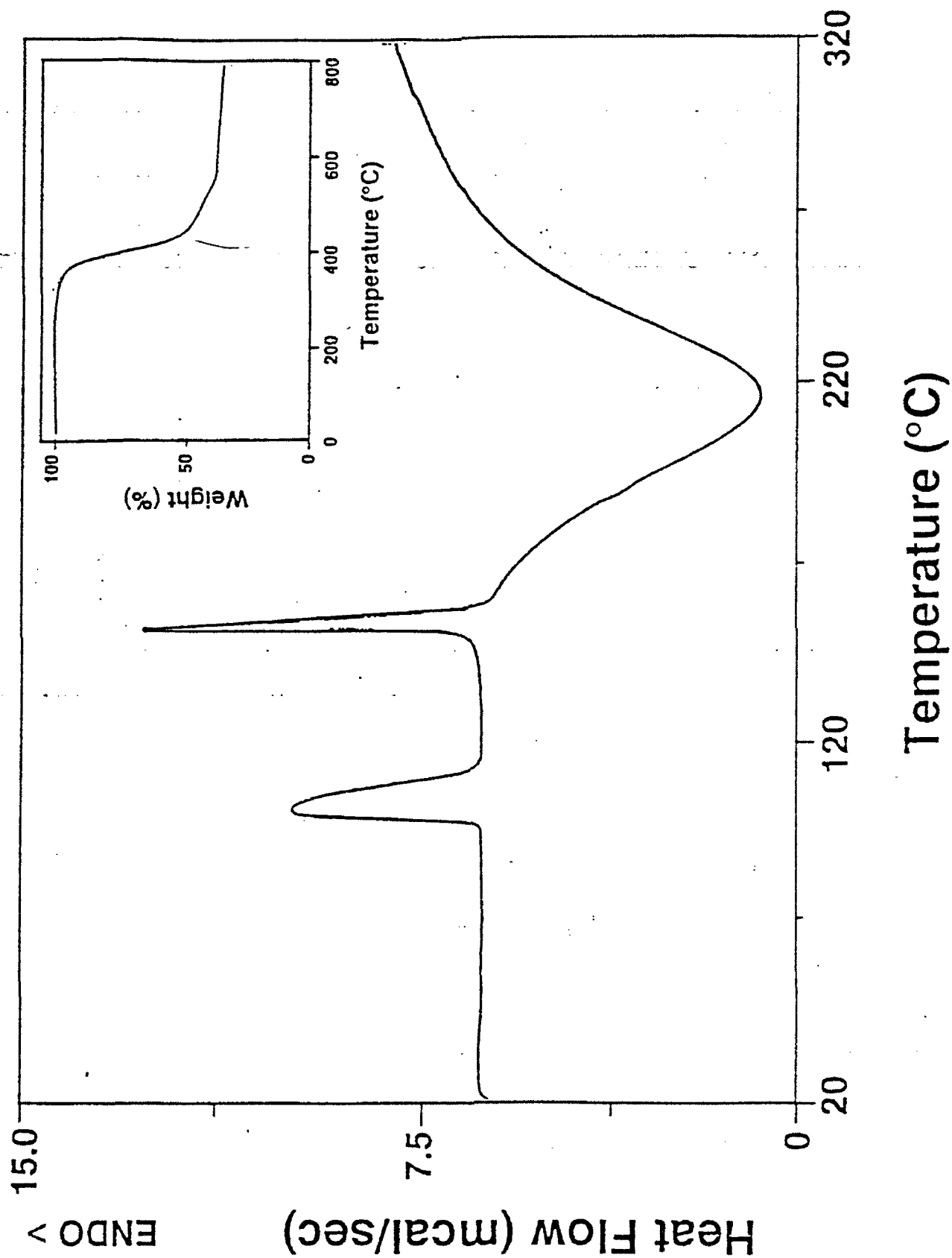


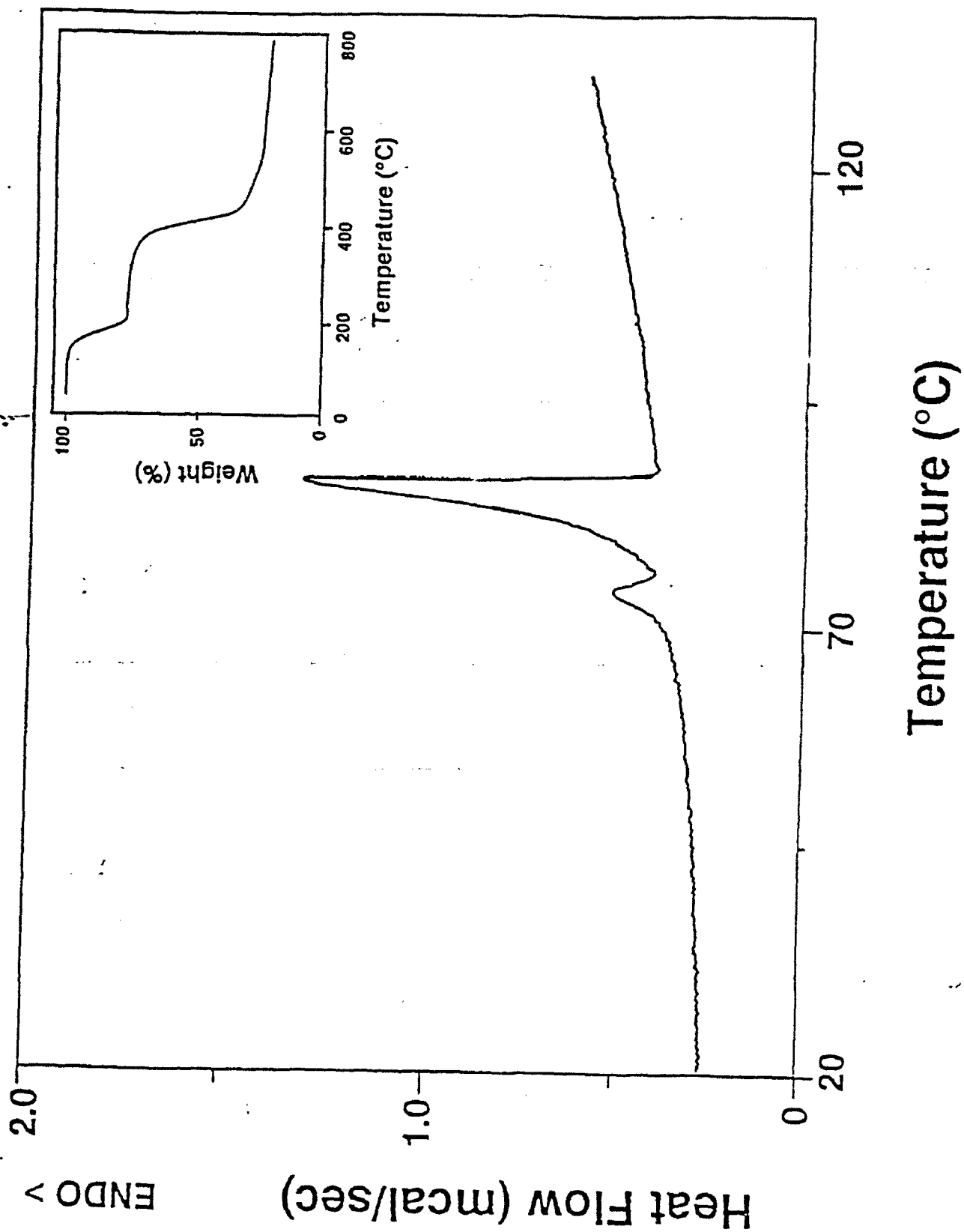
Py = pyridine; X = from terminating species

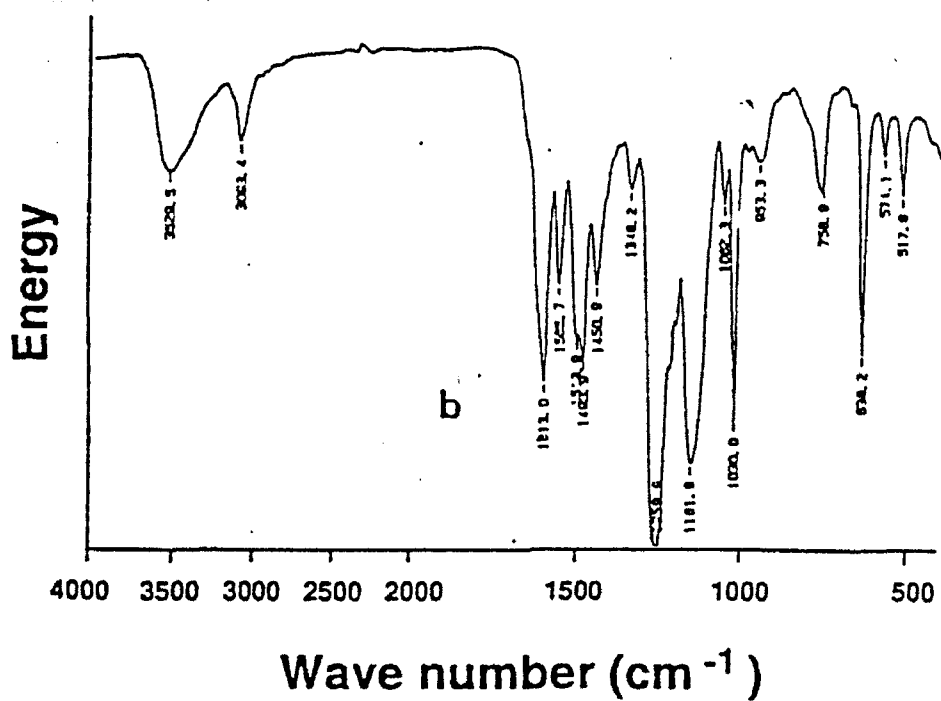
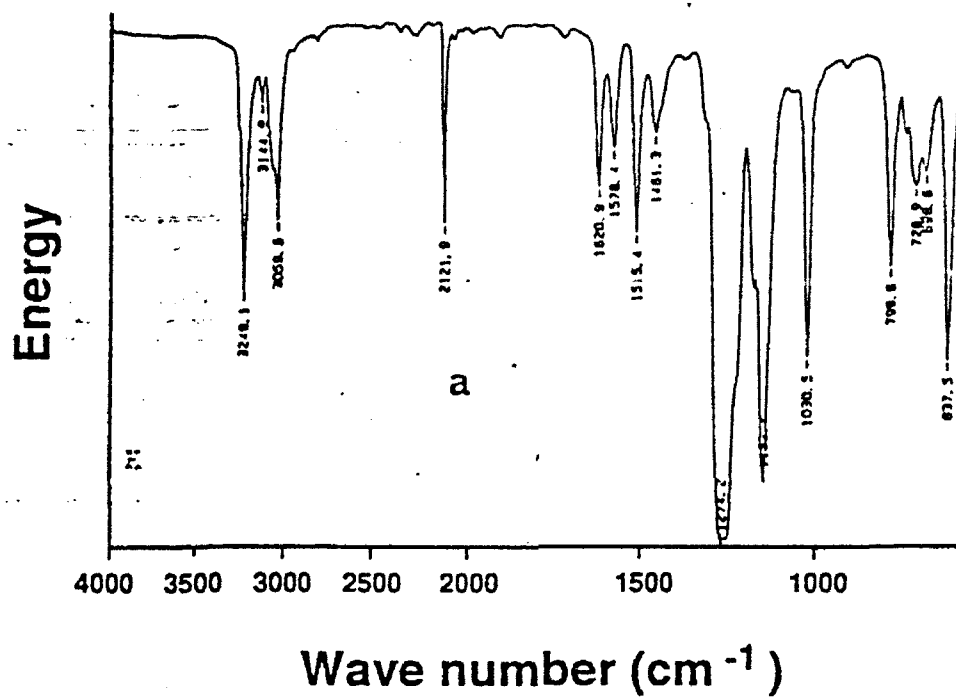


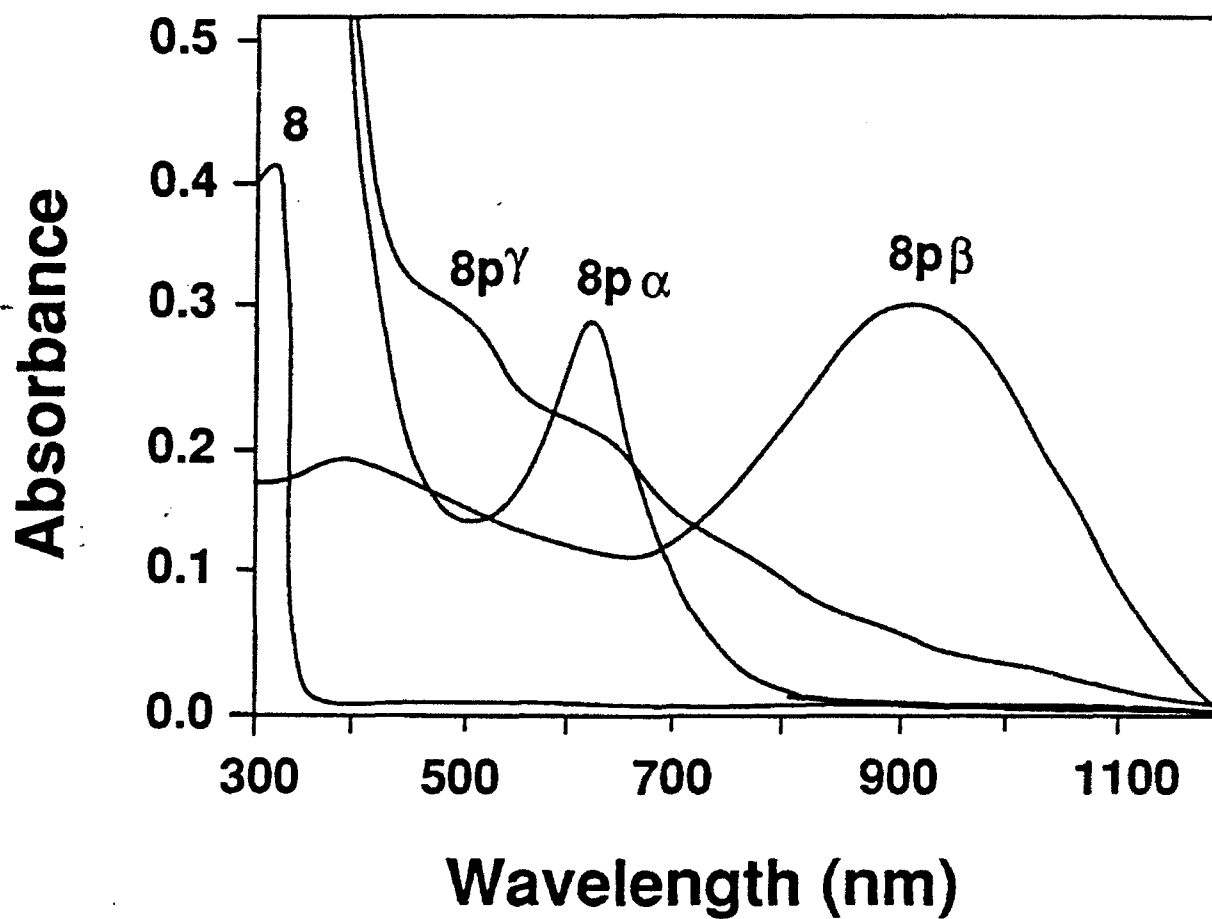
8p : R = H

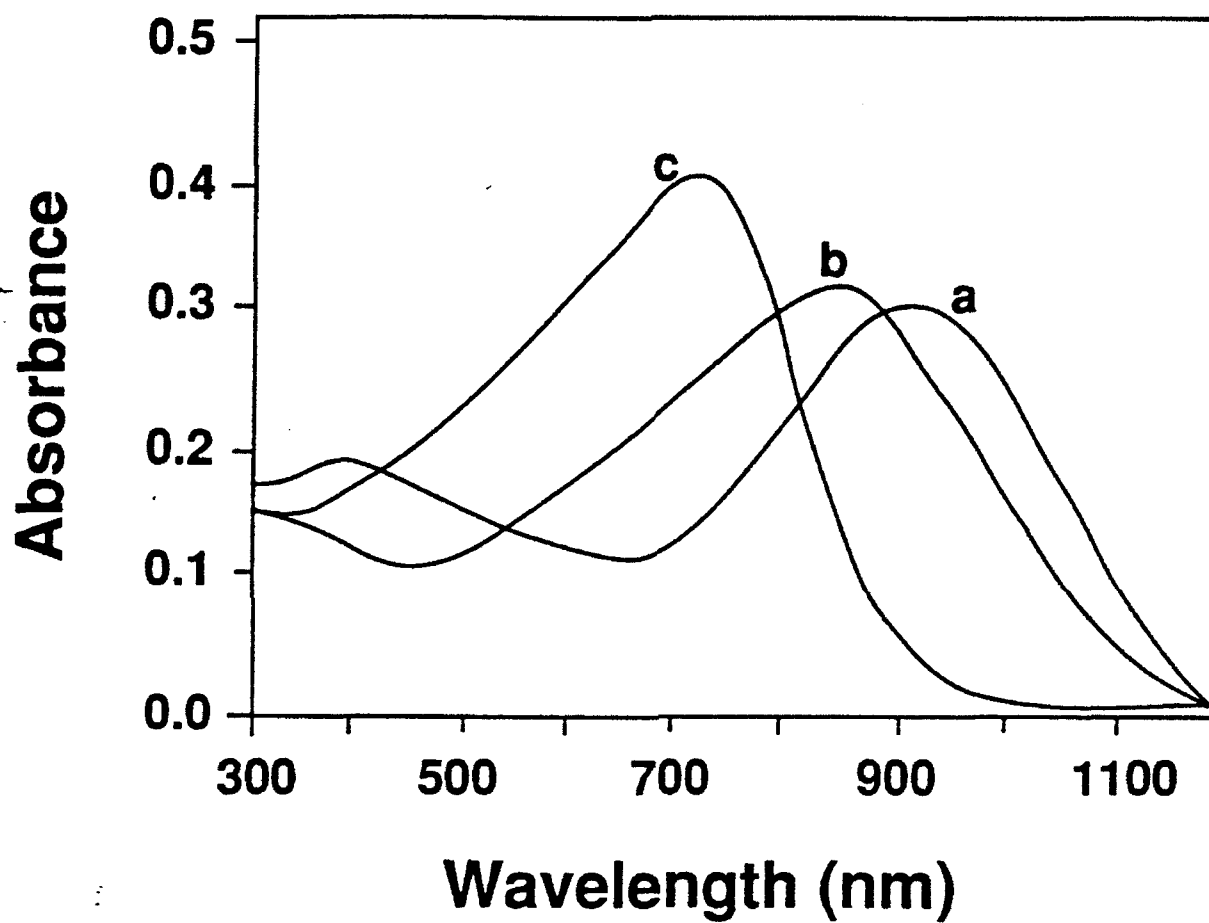
9p : R = Si(CH₃)₃











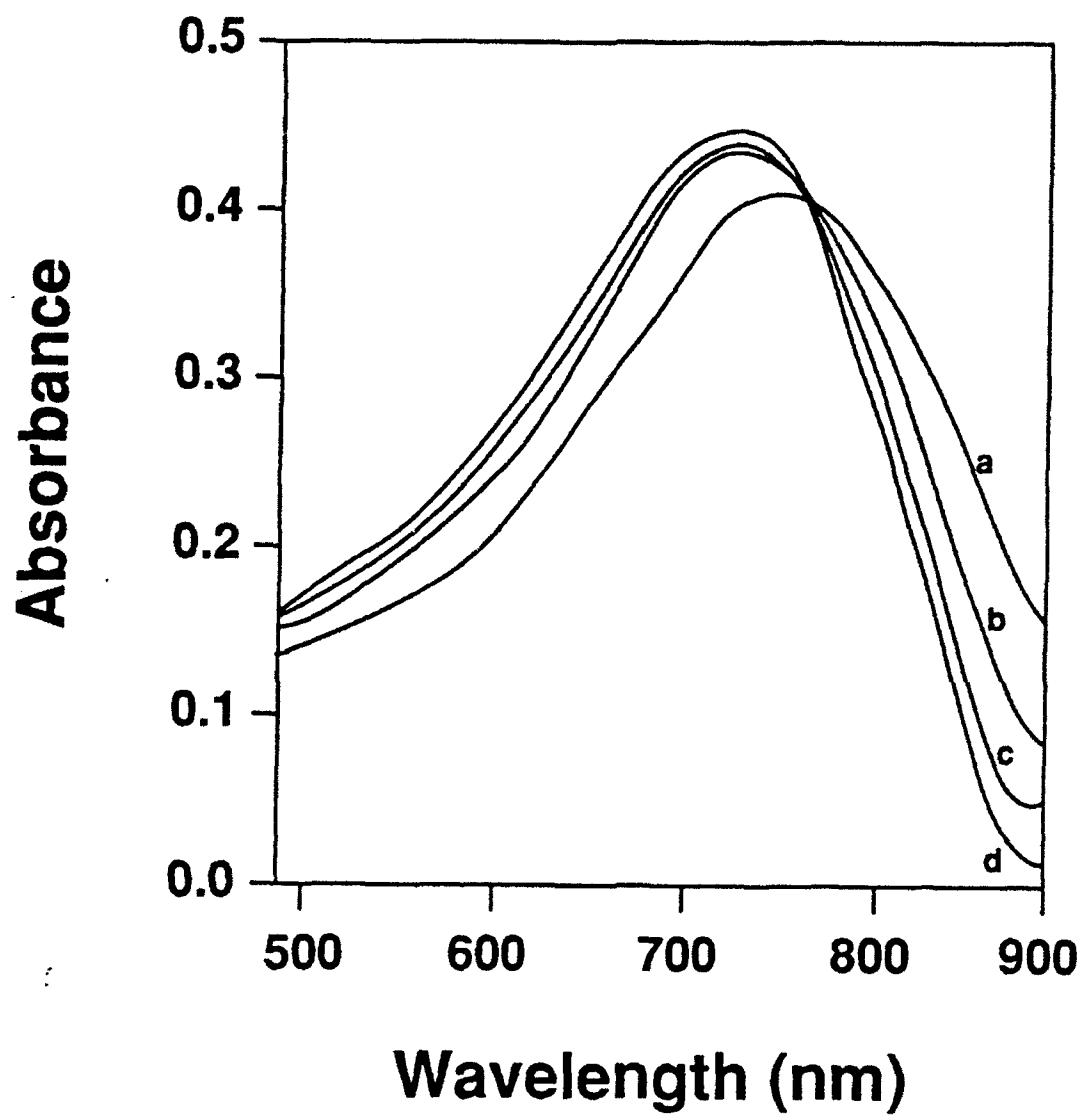


Fig 7

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Technical Report No. 2

**Conjugated Ionic Polyacetylenes 5. Spontaneous Polymerization of
2-Ethynylpyridine in a Strong Acid**

by

Sundar Subramayam and Alexandre Blumstein

Macromolecules, 25, 4,058-4,064 (1992)

University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

May 6, 1993

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Conjugated Ionic Polyacetylenes. 5. Spontaneous Polymerization of 2-Ethynylpyridine in a Strong Acid¹⁻⁵

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ABSTRACT: The spontaneous polymerization of the acetylenic bond in 2-ethynylpyridine in concentrated hydrochloric acid resulted in a substituted, extensively conjugated ionic polyacetylene bearing protonated pyridinium side groups. The conjugation length for the polymer was much greater than those obtained by spontaneous processes via a Menschutkin reaction or by complexation with bromine. Base-catalyzed deprotonation of the polymer resulted in a substantial decrease in backbone conjugation. The physical and spectral data prior to and after deprotonation correlate well with calculated values and provide insight into the structural and conformational characteristics of the polymer.

Introduction

In a series of recent papers, we have reported a new family of mono- and disubstituted ionic polyacetylenes that possess extensive backbone conjugation.¹⁻⁵ Such conjugated structures for disubstituted polyacetylenes were hitherto unreported. The polymerization reaction involved activation of the acetylenic triple bond in ethynylpyridine and its derivatives by quaternization via a Menschutkin reaction^{3,4} or by formation of donor-acceptor complexes with bromine.⁵ Figure 1 shows the activated monomers obtained in these reactions. Both methods were, however, limited by relatively low molecular masses (~4000) for the product polymers. The reaction mechanism in these spontaneous processes is an ionic one, since radical inhibitors do not affect the polymerization. The overall process is similar to that observed for the spontaneous polymerization of 4-vinylpyridine upon quaternization by alkyl halides.^{6,7}

The low molar masses for these ionic polyacetylenes obtained via quaternization may be attributed to relatively slow activation of the triple bond (which results in a low concentration of the activated species) compared to rapid propagation and termination steps. Fife et al. have shown that the quaternization of 4-vinylpyridine by ethyl bromide or ethyl tosylate is a rather slow reaction with $t_{1/2} = 1000$ min.⁸ In view of this, an alternative method was sought for a more rapid activation of the monomer. Such methods involve use of a highly reactive quaternizing agent in high concentrations.

In this paper, we report the polymerization of 2-ethynylpyridine by a strong acid. The reaction of 2-ethynylpyridine in concentrated hydrochloric acid resulted in spontaneous polymerization of the acetylenic triple bond giving a highly conjugated, ionic polyacetylene. The proposed structure for the polymer is illustrated in Figure 2.

Experimental Section

Materials. 2-Ethynylpyridine was obtained from Farchan Laboratories and distilled under vacuum before use. Concentrated hydrochloric acid was obtained from VWR Scientific Co. and used as received.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrometer using KBr plates. UV absorption spectra were obtained at 22 °C in DMSO and chloroform on an IBM 9420 visible-ultraviolet spectrophotometer. Thermal analyses were carried out on a Du Pont TGA 2950 thermogravimetric analyzer. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahren flat-plate camera using Ni-filtered Cu K α radiation. Dilute-solution viscosity measure-

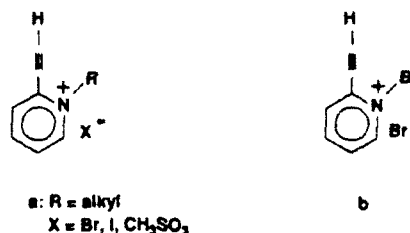


Figure 1. Activated 2-ethynylpyridine monomers obtained by (a) a Menschutkin reaction and (b) a complexation reaction with bromine.

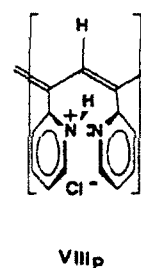


Figure 2. Proposed structure for conjugated, ionic polyacetylene resulting from spontaneous polymerization of the acetylenic triple bond of 2-ethynylpyridine.

ments were made in DMSO and chloroform at 25 °C using a Cannon-Ubbelohde dilution type viscometer. Molecular weight determination by vapor pressure osmometry was made on a UIC Inc. 070 vapor pressure osmometer in chloroform at 30 °C. Calibration was done with low molecular weight polystyrene ($M_n = 2000$) with an estimated error of $\pm 5\%$. Fluorescence spectra were obtained on a Perkin-Elmer MPF-44B fluorescence spectrophotometer equipped with a PE 150 xenon source in conjunction with a Stanford Research System Model SR440 DC 300-MHz amplifier and a SR400 two-channel gated photon counter. All spectra were recorded in DMSO at 22 °C. Excitation wavelengths of 360 and 265 nm respectively were used for the protonated and deprotonated form of polymer VIIIp. Elemental analyses were performed at Atlantic Microlabs, Atlanta, GA.

Poly(2-pyridinium hydrochloride-2-pyridylacetylene) Copolymer VIIIp. To neat 2-ethynylpyridine (2.06 g, 0.02 mol) stirred at 0 °C was added dropwise concentrated hydrochloric acid (0.71 g, 0.02 mol). An exothermic reaction ensued, and the reaction mixture acquired a dark color immediately accompanied by a rapid increase in viscosity. The polymer separated out as a black solid mass. It was washed repeatedly with ether and dried overnight in vacuum at 40 °C. The dry polymer was obtained as a lustrous black powder (2.0 g) that was readily soluble in water and DMSO but insoluble in chloroform.

IR (cm⁻¹): 3414 (br, hydrogen-bonded ring =NH stretch), 1617 (backbone C=C stretch), 1605 (aromatic ring C=C stretch). UV: λ_{max} C=C (nm) 530. η_{inh} : DMSO (dL/g) 0.2. Anal. Calc: C, 70.88; H, 4.61; N, 11.81; Cl, 12.70. Found: C, 70.25; H, 4.82;

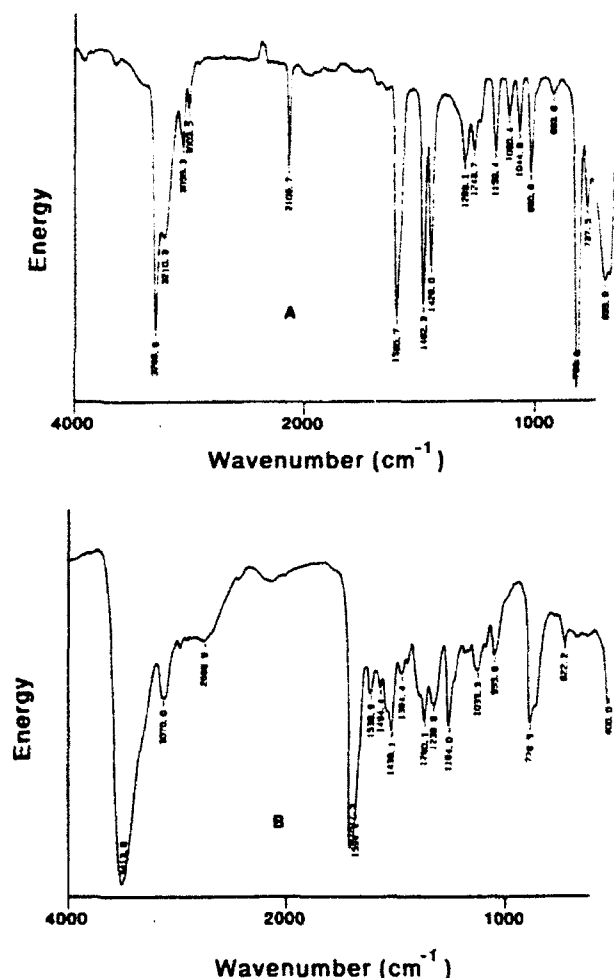


Figure 3. Infrared spectra of (A) 2-ethynylpyridine and (B) polymer VIIIp.

N, 11.80; Cl, 12.75.

Deprotonation of Poly(2-pyridinium hydrochloride-2-pyridylacetylene) Copolymer. The protonated polymer VIIp (1.0 g) was dissolved in 50 mL of deionized water, and to the stirred solution was added slowly 100 mL of 1 M KOH. Stirring was continued for 12 h, during which time the deprotonated polymer precipitated out as a dark solid. This was extracted with chloroform, and the combined organic layers were dried and the solvent evaporated under reduced pressure to yield a lustrous black solid. This was dried overnight in vacuum at 40 °C. The dry polymer (0.5 g) was soluble in chloroform and DMSO but insoluble in water.

IR (cm^{-1}): 1634 (C=C), 1585 (aromatic C=C). UV: λ_{max} C=C (nm) 419. η_{inh} : DMSO (dL/g) 0.2. Anal. Calc: C, 79.27; H, 4.82; N, 13.20; Cl, 2.71. Found: C, 75.20; H, 4.67; N, 12.33; Cl, 3.01.

Results and Discussion

The polymer obtained by the bulk polymerization of 2-ethynylpyridine in concentrated hydrochloric acid is a black lustrous solid indicative of the highly conjugated nature of the backbone (Figure 2). This is evident from its infrared spectrum, which reveals a strong absorption band at 1617 cm^{-1} due to the C=C stretch from the backbone carbons. Furthermore, the $\text{C}\equiv\text{CH}$ and $\text{C}\equiv\text{C}$ stretching bands at 3290 and 2108 cm^{-1} , respectively, that are present in the monomer are absent in the product polymer (Figure 3). The highly charged nature of the polymer is evidenced by the broad, intense band at 3400 cm^{-1} that arises from the =NH stretch of the side-group pyridinium rings and is indicative of the strong hydrogen-bonding effect due to the charged nature of the side groups. This band is characteristic of all polymers reported by us

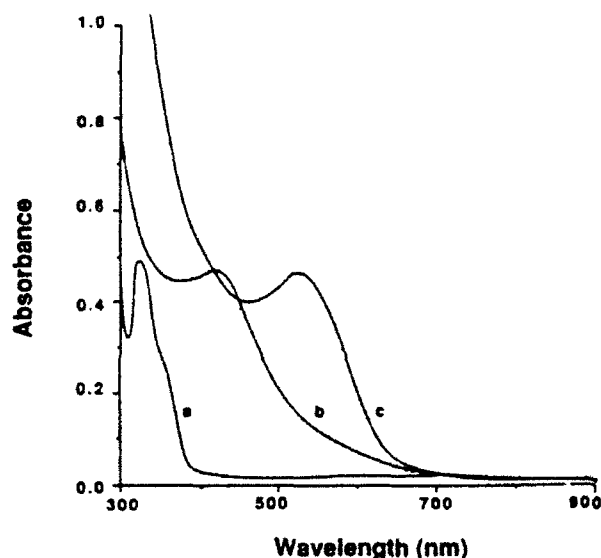


Figure 4. UV-visible spectra of (a) monomer and polymer VI-Iip in the (b) deprotonated and (c) protonated forms.

previously possessing similar structures, including disubstituted polyacetylenes.³⁻⁵ The UV-visible spectrum of polymer VIIp showed a strong absorption centered at 530 nm resulting from the $\pi\text{-}\pi^*$ transition of the conjugated polymer backbone. Figure 4 shows the UV-visible spectra of the monomer and polymer VIIp. The polymer is soluble in DMSO and in water but not in chloroform, which is characteristic of its ionic nature.

The present polymerization can be compared to that of 4-vinylpyridine in concentrated acids reported by Salamone⁹ and later by Ringsdorf.^{10,11} The former study concluded that an ionic mechanism is unlikely in such strongly protic media and that the polymerization probably proceeds by a step-growth process. The latter study proposed a mechanism wherein the polymerization of the protonated vinylpyridine occurs in an ordered array of the pyridinium halide molecules. The polymerization of 2-ethynylpyridine also occurs in the protonated monomer which activates the acetylenic triple bond. Since the spontaneous polymerization occurs only in the presence of excess unquaternized monomer (no polymerization was observed when monomer was added to excess acid), we conclude that the initiation step occurs via the nucleophilic addition of unquaternized monomer to the triple bond of the quaternized activated species. This is also supported by the fact that the isolated monomer salt failed to undergo polymerization in concentrated HCl. The propagation step, therefore, appears to proceed in a manner analogous to that suggested by Ringsdorf et al., wherein immediate termination via protonation does not occur. The molecular mass of polymer VIIp is, however, low ($\eta_{\text{inh}} = 0.2$ dL/g) suggesting that termination step(s) compete effectively with chain propagation.

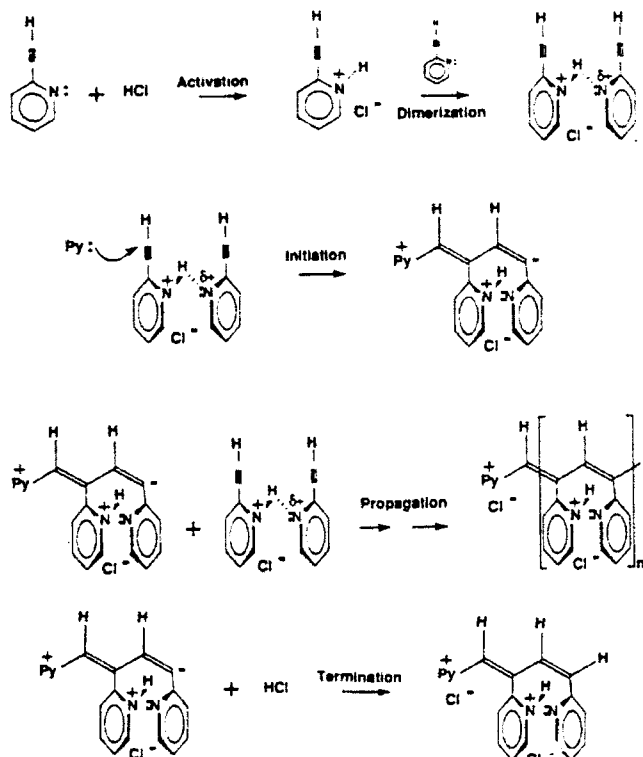
A unique characteristic that distinguishes the present polyacetylene from the ones obtained by us via the Menschutkin reaction or complexation with bromine is that, unlike the previously described systems wherein the charged side groups consist of either alkylpyridinium or bromopyridinium moieties, it has protonated pyridinium ring substituents. This allows for relatively easy deprotonation of the ionic polyene in basic media, giving rise to a largely neutral species. Such a transformation in the previously reported materials would involve drastic conditions and elevated temperatures at which polymer degradation becomes a serious problem.

Table I
Elemental Composition (%) of Poly(2-pyridinium
hydrochloride-2-pyridylacetylene) Copolymer before and
after Deprotonation by Base

	mol formula		C	H	N	Cl
prior to deprotonation	$[\text{C}_{14}\text{H}_{11}\text{ClN}]_n$	calc	70.88	4.61	11.81	12.70
		found	70.25	4.82	11.80	12.75
treated with KOH	$[\text{C}_{14}\text{H}_5(0.1)\text{-ClN}]_n^a$	calc	79.27	4.82	13.20	2.71
		found	75.20	4.67	12.33	3.01

^a Assuming 10% residual chloride ions.

Scheme I



Py = unquaternized monomer

The analytical data of polymer VIIIp fit remarkably well with a structure wherein only 50% of pyridine rings in the polymer contain quaternary nitrogens (Table I). These results imply the incorporation of unquaternized monomeric units in the polymer chain even prior to deprotonation of the pyridinium ring side groups. A possible explanation for this could be the formation of a dimeric complex between a protonated and an unprotonated monomeric species via intermolecular hydrogen bonding. This would then provide sufficient activation for the triple bond in the unquaternized molecule for it to undergo polymerization. Scheme I illustrates the proposed reaction mechanism for the polymerization. Such dimer formation has also been reported in partially protonated poly(2-vinylpyridine) between two adjacent pyridine side groups, one of which is protonated.¹² A charge-transfer complex polymerization mechanism is also possible via the formation of a weakly reactive charge-transfer complex biradical between the protonated and unprotonated ethynylpyridine molecules. The low molecular weight of the polymer and lack of temperature dependence of M_n , however, suggest that the latter mechanism is unlikely.

Treatment of VIIIp with aqueous potassium hydroxide solution gave a compound that possesses approximately 20% of the original charges (based on halide ion content). Table I lists the analytical data before and after deprotonation. Assuming that these residual charges are due

to charged end groups that cannot undergo neutralization, the DP of the polymer is approximately 12 ethynylpyridine units. Although the deprotonated polyacetylene retained its black color, remarkable changes were observed in its spectral properties. The UV-visible spectrum showed a large blue shift for the $\pi\text{-}\pi^*$ transition of the conjugated polymer backbone compared to the protonated form. The absorption maximum shifted from 530 nm for the protonated form to 419 nm for the deprotonated one. Figure 4 shows the change in the absorption maxima of polymer VIIIp before and after treatment with base. The large hypsochromic shift observed in the present polymer on deprotonation results from reduced conjugation presumably from backbone twist introduced upon deprotonation and is not due to a change in the pyridinium chromophore. This is substantiated by the fact that the UV-visible spectra of protonated poly(2-vinylpyridine) and neutral poly(2-vinylpyridine) do not differ much, displaying absorption maxima at 260 and 250 nm, respectively.¹² The backbone twist may be attributed to the absence of electrostatic interactions between the counterions and the pyridinium rings that were present in the protonated form, thereby resulting in the steric interaction between the side groups becoming a dominating factor. This view is also supported by the fact that the λ_{max} (C=C) for the backbone undergoes a bathochromic shift on reprotonation from 419 to 460 nm, trailing to ~ 800 nm. The deprotonated polymer is no longer water soluble but is readily soluble in chloroform due to its considerably diminished ionic character.

The reduced backbone conjugation in the deprotonated form of VIIIp is also supported by its IR spectrum, which shows a corresponding high-frequency shift of the backbone C=C stretch from 1617 to 1634 cm^{-1} . The aromatic ring C=C band shifted from 1605 cm^{-1} for the protonated form to 1585 cm^{-1} for the deprotonated one, which is identical to that observed for 2-vinylpyridine (1586 cm^{-1}).¹³ The C=N stretch of the pyridine ring occurring at 1458 cm^{-1} for the ionic form is shifted to 1467 cm^{-1} upon deprotonation, again being similar to that of 2-vinylpyridine (1472 cm^{-1}).¹³ The intense band at 3400 cm^{-1} due to the hydrogen-bonded pyridinium ring =NH stretch in the protonated form disappeared almost completely on deprotonation. Figure 5 shows the IR spectra of polymer VIIIp in its protonated and deprotonated forms. The latter spectrum contains weak but distinct bands at 3292 and 2102 cm^{-1} from the acetylenic $\equiv\text{CH}$ and C=C stretching found in the monomer. From the mechanism depicted in Scheme I, the initiating chain end of polymer VIIIp is an ethynylpyridinium unit linked through the quaternary pyridinium nitrogen. The residual bands may, therefore, be attributed to the end groups in the polymer. This was confirmed by performing an end-group analysis based on the acetylenic $\equiv\text{CH}$ stretching band. The relative intensity of this band at 3290 cm^{-1} for the starting monomer was compared with that for polymer VIIIp after deprotonation. The intensities were normalized using the β -ring bending band of the pyridine ring. This band occurs at 738 and 749 cm^{-1} for the monomer and polymer, respectively, and its intensity is unaffected by the nature of the substituent on the ring, i.e., alkynyl or alkenyl (β -ring bending for 2-vinylpyridine occurs at 745 cm^{-1}). Comparison of the infrared absorption ratio $\text{Abs}_{\equiv\text{CH}}/\text{Abs}_{\beta\text{-ring}}$ for the monomer and deprotonated polymer (2.30 and 0.24, respectively) yields a value of 9.1% for the end-group content, which is in excellent agreement with the value calculated from analytical data (10%), (see Table I).

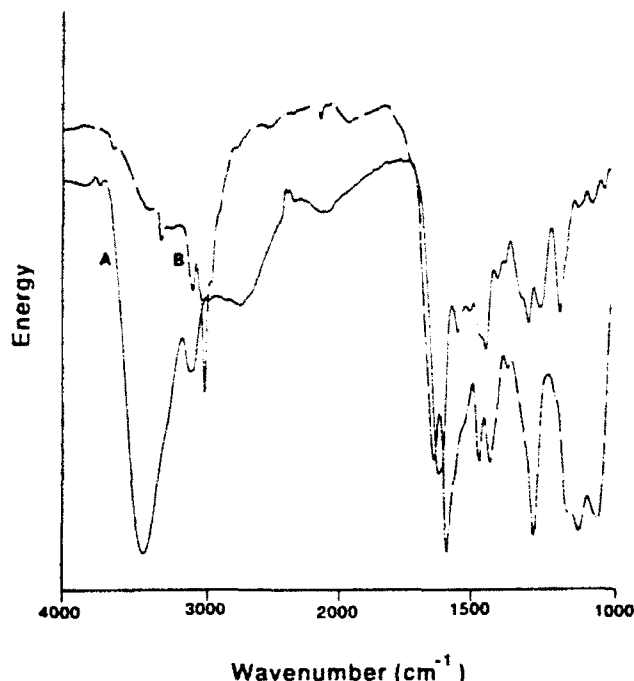


Figure 5. Infrared spectra of polymer VIIIp in its (A) protonated and (B) deprotonated forms.

TGA analysis of polymer VIIIp in a nitrogen atmosphere showed a small, gradual weight loss ($\sim 9\%$) occurring at 150°C , followed by a rapid decomposition at 230°C . The deprotonated form showed an essentially similar behavior, suggesting that the ionic nature of the polymer prior to deprotonation does not contribute significantly to its thermal stability. The decomposition temperatures are similar to those for the ionic polyacetylenes obtained by us via the quaternization method (240°C)^{3,4} and considerably higher than the ones synthesized by the formation of donor-acceptor complexes with bromine.⁵

A characteristic feature exhibited by these ionic polyacetylenes is a broad low-energy band (560 nm) in their fluorescence emission spectra. The phenomenon is attributed to intramolecular excimer formation between the aromatic side-group chromophores. It appears to be independent of the polymerization method, since the band was observed for polyacetylenes obtained via both the quaternization and complexation methods.⁵ It has also been reported for protonated poly(4-vinylpyridines)¹² and isotactic polystyrene.^{14,15} In these ionic polyacetylenes, such excimer formation is indicative of a highly conjugated backbone with minimal twist, which is a prerequisite for efficient stacking of the pyridine rings. Such stacking seems to be largely due to a strong electrostatic interaction of each counterion with two adjacent pyridinium rings.

The fluorescence emission spectrum of polymer VIIIp in DMSO, however, displayed two bands centered at 500 and 560 nm, whose intensities are similar. The intensity of the band at 500 nm was independent of polymer concentration, while that of the latter decreased slightly with increasing dilution (Figure 6a,b). This phenomenon is attributed to intramolecular excimer formation by the side-group chromophores. It is evident that two distinctly different chromophoric groups of approximately equal number (protonated pyridinium and neutral pyridine rings) are present in the polymer, substantiating the proposed structure (Figure 2) which is based on its analytical data. The band at 560 nm is assigned to the pyridinium chromophores, since it was also observed for the ionic polyacetylenes obtained by previous methods⁶

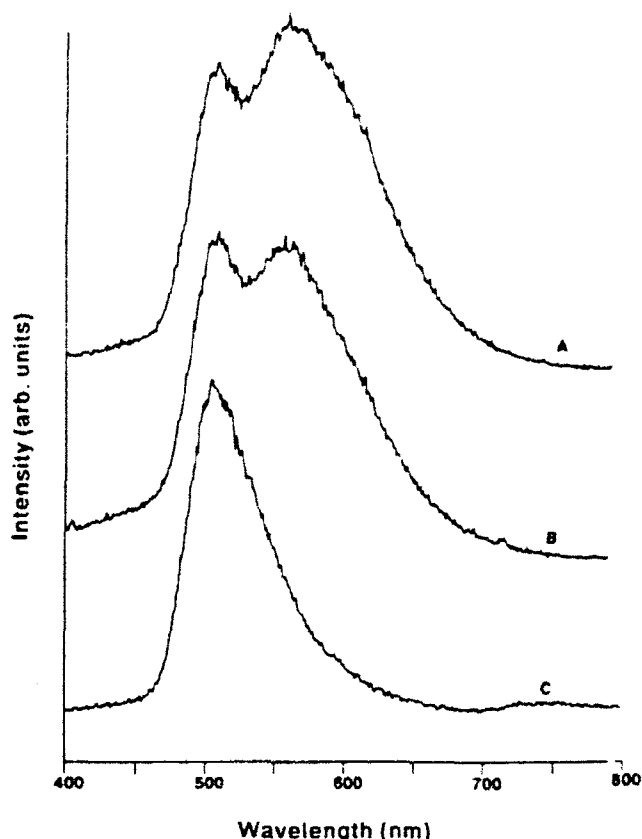


Figure 6. Fluorescence emission spectra of VIIIp: (A) 6.5×10^{-3} g/L, (B) 1.3×10^{-4} g/L, and (C) deprotonated form (6.5×10^{-3} g/L).

wherein more than 98% of the side-group pyridine rings were in the quaternized form. The emission at 500 nm is attributed to the unquaternized pyridine rings which is expected to occur at a higher frequency. This was verified by the fluorescence spectrum of the deprotonated form, which showed a single emission at 500 nm (Figure 6C). The fluorescence emission due to intramolecular excimer formation of polymer VIIIp was also confirmed by the fact that its emission spectrum at 560 nm is essentially the same as its absorbance spectrum. We believe that, unlike flexible polymers, these polyacetylenes would not lose their excimer emission at very low temperatures due to their strongly conjugated and rigid backbones that predetermine the conformation of the side-group chromophore. The configuration required for energy transfer is, therefore, built up in the polymer chains prior to excitation. Similar observations were made by Handa et al.¹² for protonated poly(2-vinylpyridine), which exhibits a "dimer-like excimer" due to interaction between protonated pyridine rings adjacent to one another. Direct measurements of fluorescence at 77 K were, however, not carried out due to instrument limitation.

The X-ray diffractogram of an unoriented sample of VIIIp indicates an amorphous scattering with a broad ring centered at $d = 11.8 \text{ \AA}$, possibly due to a layered structure. Similar diffraction patterns were also displayed by poly-(2-ethylpyridinium-acetylene iodide) obtained via the quaternization method and by poly[(2-bromopyridinium)-acetylene bromide] synthesized by the complexation method.⁵ In both cases, the broad small-angle ring occurred at $d = 11.8 \text{ \AA}$, which suggests that this layered structure is not dependent on the nature of the atom/group attached to the pyridine nitrogen located in the 2-position with respect to the polymer backbone. This reflection may be related to the ordering of the side-group

pyridinium rings which would be the case if the polymer chain adopted a trans-transoidal conformation. The effect of cis-trans stereoregularity in substituted polyacetylenes on the X-ray diffraction patterns has been reported in a recent study.¹⁶ It was found that, for poly(*tert*-butylacetylene), the *d*-spacing increases with increasing trans content from 8.5 to 10.5 Å. The diffraction pattern of deprotonated VIIIp, however, does not exhibit this characteristic ring. This is probably due to destruction of the layered arrangement caused by the increased backbone twist resulting from deprotonation. Figure 7 shows the X-ray diffractograms of the polymer prior to and after deprotonation.

The conjugation lengths based on both IR and UV-visible spectra for VIIIp are, by far, the highest observed for these ionic polyacetylenes; the spontaneous polymerization of 2-ethynylpyridine via quaternization and halogen complexation methods resulted in polymers with absorption maxima between 370 and 490 nm for the former method^{3,4} and 470 nm for the latter.⁵ The extended conjugation observed in these systems in spite of their substituted backbones is surprising and is in contrast to substituted polyacetylenes synthesized using coordination catalysts. Results obtained by us recently from modeling studies on these ionic systems using dynamic simulation methods¹⁷ indicate that both the trans-transoidal and the cis-transoidal conformations possess similar energetics and are, therefore, equally probable. The energy-minimized conformers for 10 repeat units are shown in Figure 8. The trans-cisoidal and the cis-cisoidal conformers are substantially higher in energy. It is also evident from the study that the counterions in these charged polyacetylenes interact strongly with adjacent pyridinium rings, thereby preventing backbone twisting. This is reflected by a large electrostatic energy contribution that is responsible for the stability of such conjugated conformers in these systems. This unique feature also distinguishes them from other substituted, uncharged polyacetylenes that do not possess such extended conjugation of the backbone. Our modeling study also predicts that the removal of counterions in these polymers (i.e., the uncharged state) would result in a greater backbone twist due to steric factors introduced by the substituents in the absence of the ionic interactions, leading to reduced conjugation.

A literature survey shows that the conjugation number *n* for a polyene may be estimated from the UV-visible spectra of the conjugated segment present in the polymer. This method has been applied by Dai and White,¹⁸ who have correlated the absorption maxima of conjugated segments obtained by dehydrohalogenation of iodine-doped 1,4-polyisoprene with the conjugation number *n*. Plotting *n* versus the square of the wavelength for each absorption, they obtained a straight line, indicating that the Lewis-Calvin equation, $\lambda_{\max}^2 = kn$, is obeyed fairly well.¹⁹ This relation, which has been verified for low molecular polyenes (*n* = 3–10),²⁰ was shown by these authors to be valid for *n* ranging from 4 to 11. The conjugated sequences calculated from a single value of *k* (*k* was calculated to be 17 532) gave a good correlation of expected and found values.¹⁸ The study also concluded that it was possible to predict the distribution of conjugated sequences insulated from one another from their characteristic absorption maxima for *n* values of up to 11.

In an attempt to verify the applicability of the Lewis-Calvin equation for these ionic polyacetylenes, the UV-visible absorption maxima of their conjugated backbones were correlated with the conjugation number *n*. Figure

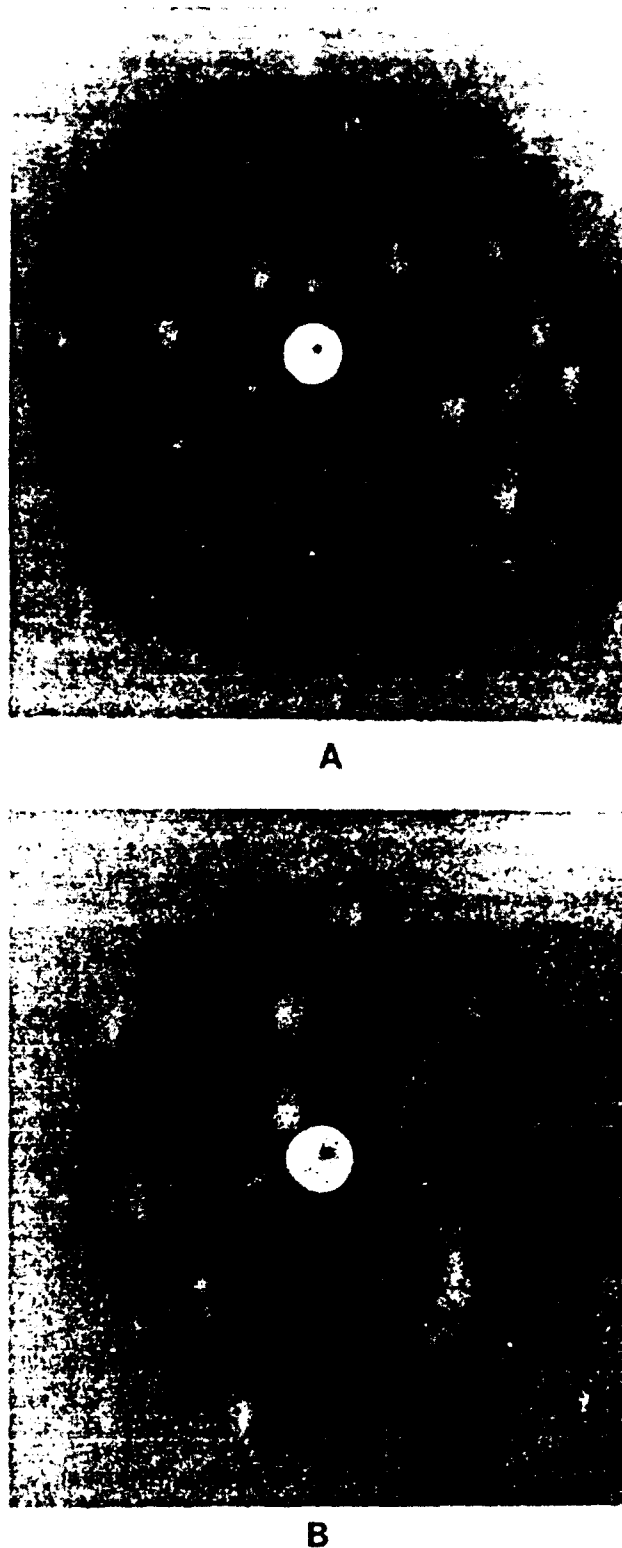


Figure 7. X-ray diffractograms of VIIIp in the (A) protonated and (B) deprotonated forms.

9 shows a plot of $\lambda_{\max}^2(\text{C}=\text{C})$ versus *n* obtained for polyenes with *n* = 3–10 that were obtained in the previous study.²⁰ Extrapolation from this plot for polymer VIIIp using its $\lambda_{\max}(\text{C}=\text{C})$ absorption maximum gave a conjugation length *n* of 16. If the proposed reaction mechanism for the polymerization that involves a nucleophilic addition to the acetylenic bond in the propagation step occurs in a trans fashion (which is commonly observed for additions across carbon-carbon multiple bonds), the product polymer would possess a fully extended, trans-transoidal conformation through the entire length of the

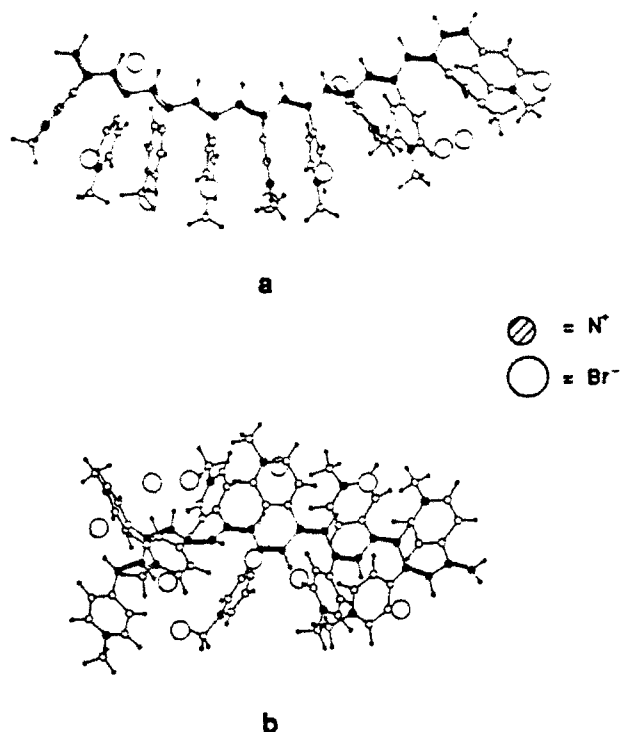


Figure 8. Energy-minimized conformers of poly(4-methylpyridinium-acetylene bromide) in the (a) trans-transoidal and (b) cis-transoidal conformations (from ref 17).

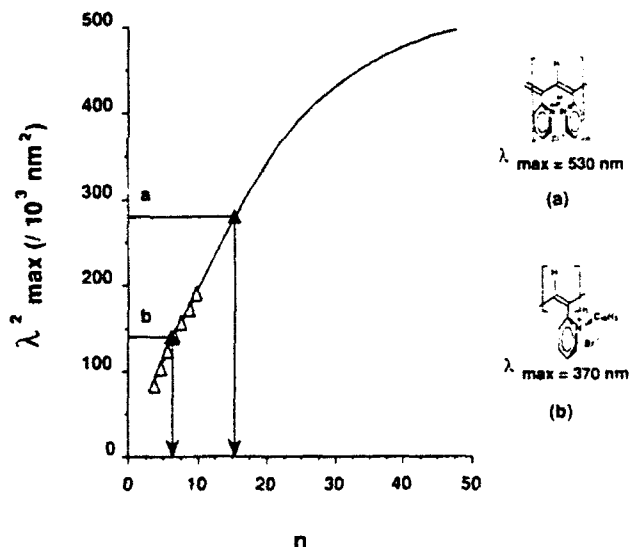


Figure 9. Plot of $\lambda_{\max}^2(\text{C}=\text{C})$ absorption maxima versus conjugation number n for polyenes: (Δ) from ref 18; (\blacktriangle) this work.

chain. Such a conformation is also predicted to be a highly stable one for these systems by our modeling studies.¹⁷ If this is true, the conjugation number n for these polymers should be equal to their degree of polymerization, DP. The validity of this assumption was verified for polymer VIIIp by comparing its calculated molecular weight (assuming $n = \text{DP}$) from the UV-visible spectra with the experimentally determined number-average molecular weight (M_n) for the deprotonated form obtained by vapor pressure osmometry (Figure 10a). The agreement between the calculated and experimental values within the error of the experiment ($\pm 5\%$) is particularly good. This suggests that these ionic systems do possess a fully extended, trans-transoidal conformation through almost the entire length of the polymer chain. The equation was also found to be applicable for poly(2-*n*-octadecylpyridi-

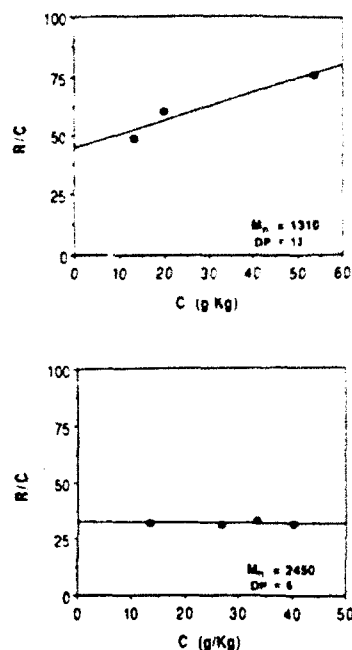


Figure 10. Plot of VPO data for (a) deprotonated VIIIp and (b) poly(2-*n*-octadecylpyridinium-acetylene bromide).

Table II
Calculated and Experimentally Determined Conjugation Numbers n and DP for Ionic Polyacetylenes

polymer	$\lambda_{\max}(\text{C}=\text{C})$ (nm)	n, DP	
		calc	exptl
	530	16 ^a 12 ^b	13 ^c
	370	8 ^a	6 ^c

^a From Lewis-Calvin equation $\lambda_{\max}^2 = kn$ (Figure 9). ^b From end-group analysis, assuming $n = \text{DP}$. ^c From VPO measurement.

nium-acetylene bromide) which was obtained by the quaternization method by making a similar comparison with its molecular weight obtained by direct determination using VPO (Figure 10b). The degree of polymerization, DP, of 12 and the molecular weight (M) of 1240 calculated from the end-group analysis for deprotonated VIIIp (based on its analytical data and IR spectrum) are also in excellent agreement with experimentally determined ones (DP = 13, M_n = 1310 by VPO). This is shown in Table II.

The validity of the Lewis-Calvin relation for the ionic polyacetylenes implies that the properties of the conjugated polymer backbones in these systems resemble those of the corresponding dimethylpolyenes for which the equation was deduced. Furthermore, it is evident from this study that the range of n over which it is applicable may be extended to an n value of up to 16. Obviously, the expression cannot be expected to be valid for high values of n , since it is known that bond alternation effects in long polyenes cause the band gap [and $\lambda_{\max}(\text{C}=\text{C})$] to asymptotically approach a constant value. Based on a band-gap energy of 2.4 eV for fully *trans*-polyacetylene, the $\lambda_{\max}(\text{C}=\text{C})$ saturates at $\sim 625 \text{ nm}$.²¹ A recent study of the

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by

S. B. Clough, X. F. Sung, S. Subramayam, N. Beladakere, A. Blumstein
and S.K. Tripathy

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Molecular Dynamics Simulation of Substituted Conjugated Ionic Polyacetylenes

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ABSTRACT: Molecular dynamics simulations were carried out on the model systems of a recently reported new class of substituted polyacetylenes possessing extensive backbone conjugation and high charge densities. Our results show that for models of these polymers with charged pyridinium substituents and bromide counterions, the polymer backbones are highly extended, which is in complete contrast to uncharged, substituted polyacetylenes. For the *trans-transoidal* conformer the counterions located between the positively charged pyridine rings have strong electrostatic attractive interactions with aromatic hydrogen atoms. It is shown that the enhanced electrostatic interactions are mainly responsible for the observed planar extended geometry in these ionic polyacetylenes. It is concluded that the Coulomb interactions play a dominant role in the conformation and dynamics of such systems.

Introduction

Substituted polyacetylenes are of considerable interest because of their stability, solubility, and easy processability. These polymers, however, lack the high degree of conjugation displayed by unsubstituted polyacetylene, making them poor conductors of electricity.¹ Significant interest in substituted polyacetylenes derives from the work by Masuda and Higashimura.¹ The lack of conjugation in these polymers is attributed to steric factors introduced by the substituents, which force the double bonds in the polymer backbone to twist out of coplanarity. This is evidenced by their spectral characteristics in the UV region that are devoid of strong absorptions in the visible range.¹ Most substituted polyacetylenes form clear transparent or yellow solutions, in contrast to the shiny metallic films of insoluble polyacetylene itself.

Severity of the steric hindrance may in fact lead to a rigid polymer which is soluble, but whose backbone can access limited conformer states.² Clough et al. have carried out extensive molecular dynamic simulations for this class of substituted polyacetylenes.² Their calculations and experimental evidence¹ tend to support a chain conformation that is noncoplanar with several restricted conformer states as the substituents become bulkier. It was shown that as side groups increase in size and number (for example polypropyne, polybutyne, and poly(*tert*-butylacetylene)), the backbone conformations become increasingly restricted and nonplanar. For poly(1-(trimethylsilyl)-1-propyne), barriers to rotation about the backbone single bond were as large as 40 kcal/mol. It was concluded that the rigid noncoplanar conformation established during synthesis will be maintained.

More recently, Subramanyam and Blumstein described the synthesis and properties of a new family of substituted polyacetylenes displaying high degrees of conjugation and possessing high charge densities.^{3,4} Their general structures are illustrated in Figure 1. These polyenes as synthesized are black solids and display large bathochromic shifts in the visible range of the electronic spectrum in comparison with the starting monomers. It is evident from the spectroscopic data that these polymers possess extensively conjugated backbones. This also confers on them a certain rigidity and brittleness. They are readily soluble and are stable up to temperatures of 250 °C analogous to polypropynes, whose structural characteristics have been

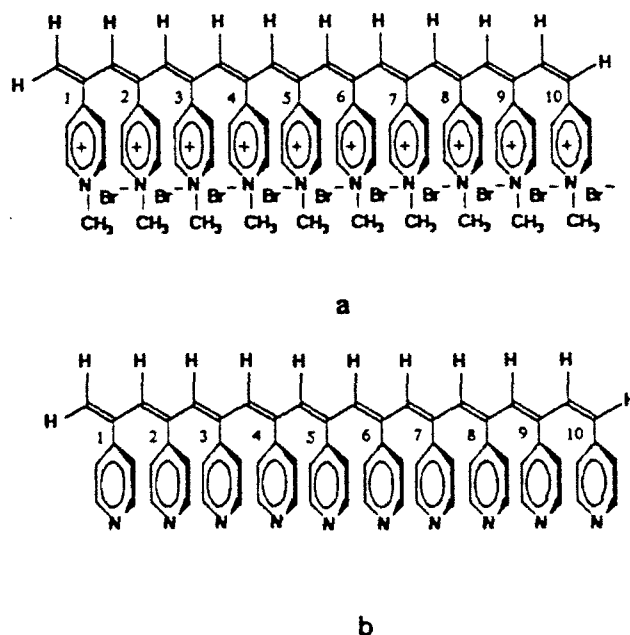


Figure 1. Substituted polyacetylene with 10 repeat units in the (a) charged and (b) uncharged states.

previously reported.¹ Doping with either donors or acceptors resulted in substantially higher conductivities (10^{-2} S/cm) compared to the undoped state ($<10^{-9}$ S/cm), which is in support of a conjugated polyene backbone for these systems.

The presently described polymers are unique with respect to their long conjugation in spite of high degrees of substitution. The extensive conjugation observed in this polymer class is surprising. It is postulated that the arrangement of the charged species in the side group architecture and the dominant Coulomb interactions play an important role in dictating the backbone conformation and dynamics. In contrast, the dispersive-repulsive forces play a dominant role in dictating the nonplanar conformations in the uncharged substituted polyacetylenes investigated earlier.²

In an effort to determine the structural characteristics responsible for these phenomena, modeling studies were extended to a representative polymeric system.² In particular, it is of interest to understand the factors

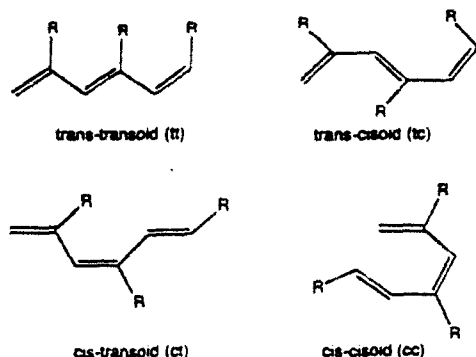


Figure 2. Various conformations of polyacetylene.

responsible for the coexistence of high degrees of substitution and extensive conjugation of the polymer chain, as well as the role played by the ionic charges in stabilization of such planar structures.

Calculations

Bond lengths, bond angles, force constants, and force field parameters employed in the present calculations were supplied by Polygen Corp. These parameters were used either as supplied or after a suitable modification, which was used in our earlier studies on dynamics simulation of substituted polyacetylenes.² Molecular mechanics and molecular dynamics results were obtained using Polygen Corp.'s QUANTA/CHARMM software on a Stellar GS1000 graphics computer in our Molecular Design Laboratory. The dynamics simulation employed the Verlet algorithm.^{5,6}

The charged and uncharged forms of the representative polymeric system (including the end groups) used in the study are shown in Figure 1. Figure 2 shows the four possible conformations of each form that were considered for the calculations.

The calculated potential energy (E_{pot}), kinetic energy (E_{kin}), and total energy (E_{total}) are given by eqs 1, 2, and 3, respectively.

$$E_{\text{pot}} = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der Waals}} \quad (1)$$

$$E_{\text{kin}} = \sum_{i=1}^N m_i \langle v_i^2 \rangle = \frac{3}{2} N k T \quad (2)$$

$$E_{\text{total}} = E_{\text{pot}} + E_{\text{kin}} \quad (3)$$

where m_i and v_i are the mass and velocity of the i th atom, respectively, N is the total number of atoms in the system, and k is the Boltzmann constant.

The polymer models were created by ChemNote in QUANTA. Calculations were performed on a chain of ten repeat units. The charges of the atoms on the side group were reassigned based on the results from AM1⁷ calculations on a model compound representing one repeat unit. The models underwent steepest descents energy minimization to remove bad contacts. The optimized structures were then heated to 300 K followed by an equilibration period. Heating was accomplished by initially assigning random velocities according to a Gaussian distribution appropriate for that low temperature and then running dynamics. The temperature was gradually increased by assigning greater random velocities to each atom at predetermined time intervals. During equilibration, the system was allowed to evolve spontaneously for a specific period of time by integrating the equations of motion until the average temperature and structure remained unchanged. Typically, runs were made with

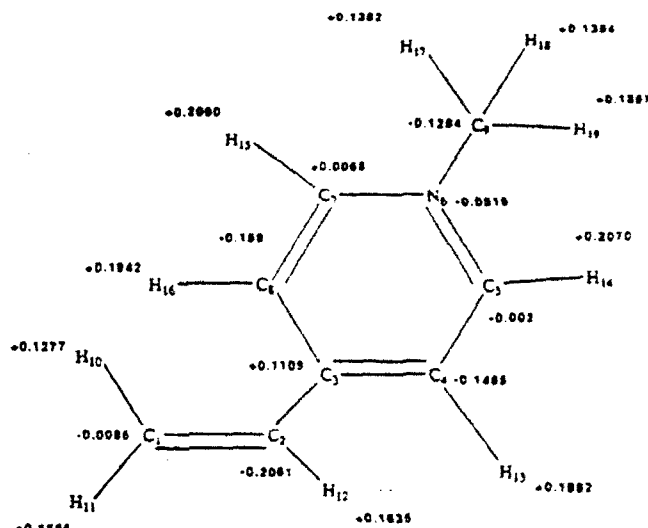


Figure 3. Charges on the individual atoms on the pyridinium ring calculated by AM1.

intervals of 50–100 ps and a step size of 1 fs. For the charged polymer, an additional 200 ps of dynamics simulation was carried out on the trans-transoid (tt), trans-cisoid (tc), cis-transoid (ct), and cis-cisoid (cc) conformers. Additionally, 2400 ps of simulation was performed on selected structures.

Results and Discussion

Charge Distribution. The AM1 method was used to calculate the charges on the individual atoms for the model compound representing one repeat unit (Figure 3). The hydrogen atoms bonded to the ring have the highest positive charge (0.2), while those of the *N*-methyl groups have a smaller value (0.14). A charge of -1 was assigned to each Br^- ion. Further, the results indicate that the substituent (ethyl or ethylene) at the para position with respect to nitrogen has little effect on the charge distribution in the ring and the *N*-methyl group. When defining the charge distribution for the polymer, two hydrogen atoms (one each from carbons C_1 and C_2) were deleted, which resulted in the polymer being negatively charged. To make the system electrically neutral, the charge on carbon C_2 in the resulting ethylene group was, therefore, changed arbitrarily from -0.2061 to $+0.02$.

The charge distribution as calculated by AM1 was extended to the ionic polyacetylene shown in Figure 1a containing ten repeat units for three conformations, namely, trans-transoid (tt), trans-cisoid (tc), and cis-transoid (ct). As expected, the cis-cisoid (cc) conformer had slightly higher energy, with the chain coiling back on itself, and is omitted in further discussions. The chain conformations of the tt and ct forms with the associated counterions after 300 ps of dynamics simulation is shown in Figure 4. The Br^- anions that were arbitrarily placed in the plane of the polyene backbone prior to the simulation underwent a positional change during the dynamics simulation, as is evident from the figure. The location of the anion prior to and after simulation for the ct conformer is illustrated in Figure 5.

In the tt conformer, the Br^- ions underwent a positional change (with respect to their initial placement) such that they are displaced from the plane of the polyene backbone. They are closely associated with aromatic ring hydrogens of adjacent pyridinium rings (Figure 4a). There are 24 close Br^- -H interaction pairs whose average distance is less than 3 Å. Twenty of these are from Br^- -H_{aromatic} pairs

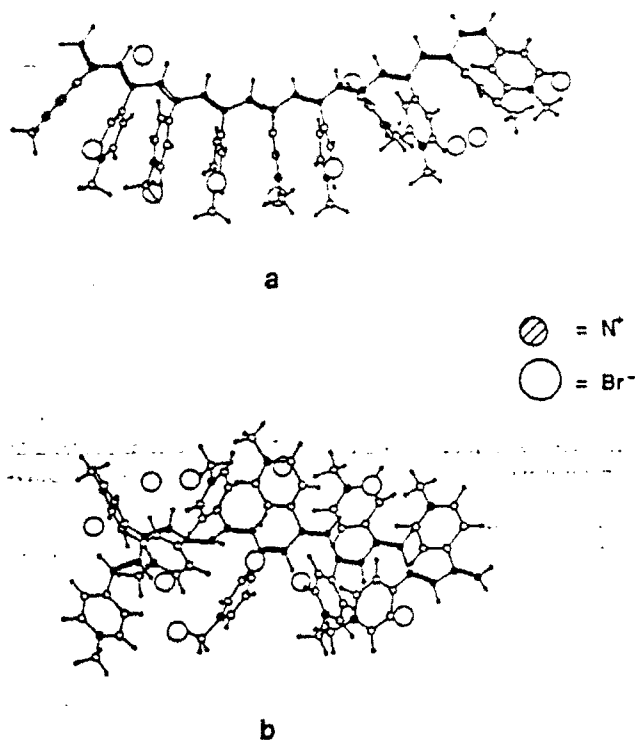


Figure 4. Chain conformations of (a) tt and (b) ct conformers with associated counterions after 300-ps dynamics simulation.

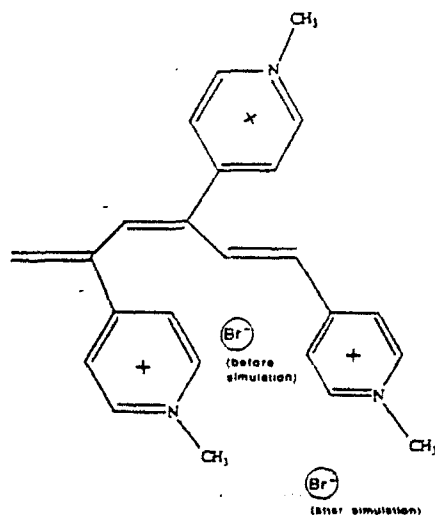


Figure 5. Position of Br^- ion with respect to the pyridinium rings before and after simulation for the ct conformer.

and four are from Br^- - $\text{H}_{\text{methylene}}$ pairs. There are no interaction pairs involving Br^- - H_{methyl} pairs; this is attributed to the repulsion between the anions that would occur if they were to be spatially situated for such an interaction. In the ct conformer, the Br^- anions were also displaced from their initially assigned position after dynamics simulation. However, in contrast to the tt conformer, they are located closer to the *N*-methyl groups for the ct conformer (Figure 4b), resulting in strong attraction with the methyl hydrogens. It was also observed that the Br^- and the methyl hydrogens exhibit strongly correlated motions. (The distance between two methyl groups on adjacent pyridinium rings was calculated to be 6.3 Å.)

It was observed that the average distance between a Br^- ion and the H atoms on the pyridine rings (numbered 13, 14, 15, and 16 in Figure 3) is in the range 2.63–2.91 Å for all the conformers being discussed, with fluctuations in the range 0.13–0.23 Å. No significant fluctuations in the

backbone rotation were observed after 2400 ps of simulation performed on selected conformers.

Simulations were also carried out on the corresponding polymeric system on the corresponding uncharged polymer, i.e., with the charges "turned off", as well as a charged system with excess Br^- ions (20 Br^- for 10 repeat units of the polymer). The latter is analogous to a doped system. The calculated energies and the various components of these energies are listed in Table I. It is evident from the large increase in $E_{\text{electrostatic}}$ that attractive electrostatic interactions increase substantially upon introduction of charge compared to the uncharged system. The charged side groups with the associated counterions in the ionic polyacetylene, therefore, play a significant role in stabilizing an extended, planar backbone conformation in such systems. The data also suggest that introduction of excess Br^- ions leads to an additional increase in the electrostatic component, indicating greater stabilization of such planar conformations in doped systems. The irreversible dopant uptake of, e.g., iodine observed for these polymers⁶ supports this inference.

Chain Conformation. The computed energies listed in Table I have been used for chain conformation comparisons for the tt, ct, and tc conformers. The average calculated energies for all three conformers were similar and were within a difference of only ~ 5 kcal/mol, per repeat unit. The average fluctuation of the dihedral angles and the rotations of the backbone single and double bonds from planarity are shown in Table II. It is observed that for each of these structures, the deviation of the backbone conformation from planarity is not significantly large. Also, the average deviation of the dihedral angle from planarity for the backbone single bond is smaller for the charged polymer than that for the uncharged one, which is indicative of an additional stabilization of the planar structure in the charged polymer. This deviation is also smaller than those calculated for polyacetylenes substituted with uncharged bulky side groups.²

An alternative method was also employed to confirm the extended chain structure in these ionic polyacetylenes. It involved an estimation of the end-to-end distance of the chains of finite length (ten repeat units). The end-to-end distance is defined by the length of the straight line joining the mass centers of the two end groups of the model polymers. This distance was estimated to be between 19 and 21 Å for all three conformers that were investigated, which is indicative of an extended conformation. This observation is also consistent with the spectral characteristics of these polymers, which confirm an extended backbone π conjugation.

The relative distances and orientations of the side group pyridinium rings with respect to each other in these ionic polyacetylenes was also estimated. Such estimates were obtained for both the charged and uncharged polyene (i.e., with the charges "turned off") and are listed in Table III. It is evident that the distances between the mass centers of any two neighboring rings generally increase when the charges are "turned off", since the steric factors force them away from one another. This results in a loss of planarity of the polymer backbone with a concomitant loss in chain extension.

The average dihedral angles between the backbone and the side group pyridinium rings are approximately 19, 32, and 57° (from 90°) for the tt, ct, and tc conformers, respectively, where 90° indicates that the ring plane is orthogonal to the backbone. The simulations suggest planar stacking of the aromatic side groups for the tt conformer (Figure 4a). The substantially larger dihedral

Table I
Components of the Potential Energy^a of the Model Systems with 10 Repeat Units

model type (tt)	E_{total}	E_{elec}	E_{vdw}	E_{bond}	E_{angle}	E_{dihed}	E_{impr}
uncharged model	167	-15	28	31	44	46	33
charged model with 10 Br ⁻	26	-183	22	33	61	54	39
charged model with 20 Br ⁻	-126	-323	11	33	61	57	35

^a In kcal/mol per repeat unit.

Table II
Average Backbone Rotation and Dihedral Angle Fluctuation for Various Conformers

conf	av backbone rotation (deg)				av dihedral angle fluct (deg)			
	single bond		double bond		single bond		double bond	
	chr	unchr	chr	unchr	chr	unchr	chr	unchr
tt	6.9	21.2	3.6	8.2	7.3	8.2	5.0	5.2
tc	18.5	13.8	9.3	7.5	6.9	9.1	4.7	5.2
ct	20.6	30.3	7.2	5.2	8.2	12.8	5.2	5.9

Table III
Distance between Mass Centers of Pyridine Rings for Charged and Uncharged States

conf	ring no. ^a	dist between mass centers (Å)	
		chr	unchr
tt	1 and 2	3.26	3.97
	2 and 3	3.53	4.87
	3 and 4	3.29	4.91
	4 and 5	3.53	5.15
	5 and 6	3.28	5.07
	6 and 7	3.54	4.98
	7 and 8	3.18	3.67
tc	1 and 2	5.03	6.28
	2 and 3	5.44	5.86
	3 and 4	5.61	6.09
	4 and 5	4.27	5.96
	5 and 6	3.47	5.92
	6 and 7	4.30	5.98
	7 and 8	4.72	6.29
ct	1 and 2	5.63	6.79
	2 and 3	4.90	6.34
	3 and 4	4.93	6.01
	4 and 5	5.48	6.27
	4 and 6	4.52	4.85
	6 and 8	3.97	4.91
	7 and 8	5.28	6.08

^a The ring numbers correspond to the numbering scheme indicated in Figure 1.

angle for the tc model (i.e., 57° from orthogonal) is consistent with larger deviations of the backbone from planarity. The fact that the charged polymer model investigated in this study displays a long-wavelength fluorescence band in its emission spectrum⁹ due to intramolecular excimer formation between the pendant

aromatic rings is indicative that the tt conformation is favored over the ct and tc conformers in these ionic polyacetylenes.

Conclusions

The present study shows that the preferred chain conformations of substituted polyacetylenes with ionic side groups that are associated with counterions are planar and highly extended. They resemble unsubstituted polyacetylene in this regard but are in complete contrast to their counterparts where the substituents are uncharged and bulky. In unsubstituted polyacetylene, the backbone π conjugation plays an important role in dictating the planar extended structure as the preferred conformation. In uncharged substituted polyacetylenes, the steric interaction of the side groups plays a dominant role in dictating a rigid but nonplanar backbone conformation without π conjugation. In the presently described systems, the electrostatic attractive interactions between the charged side groups and the counterions override the steric repulsive interactions between side groups, resulting in an extended and planar geometry for the backbone.

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Technical Report No. 4

**Polymerization of ethynyl pyridinium triflates:
Ionic polyacetylenes with extensively conjugated backbones**

by

Sundar Subramayam and Alexandre Blumstein

ACS Polymer Preprints, 33, 2, 196 (1992)

University of Massachusetts Lowell
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May 6, 1993

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<p>A new route for polymerization of the acetylenic bond in ethynylpyridines is described. Unlike previous methods wherein quaternization resulted in spontaneous polymerization of the acetylenic bond, the present method affords isolation of the activated monomeric species in the form of alkylpyridinium salts. Polymerization of the activated monomers when initiated with nucleophiles such as pyridine resulted in substituted, ionic polyacetylenes with extensively conjugated backbones.</p>					
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POLYMERIZATION OF ETHYNYLPYRIDINIUM TRIFLATES: IONIC POLYACETYLENES WITH EXTENSIVELY CONJUGATED BACKBONES

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Introduction:

Substitution at the backbone carbons of polyacetylene with various groups offers advantages of better processability and greater oxidative stability compared to unsubstituted polyacetylene, but results in substantial lowering of electrical conductivity and third order non linear optical susceptibility (χ^3). This is mainly due to loss of conjugation arising from twisting of the polymer backbone as a result of unfavorable steric interactions between the substituents.

We have recently reported the synthesis of a new class of mono and disubstituted ionic polyacetylenes with extensively conjugated backbones (1-6). The structural features of these polymers are unique with respect to their ionic nature, high degrees of substitution and extensive backbone conjugation. These polymers contain pyridinium ring substituents that are associated with halide or methanesulfonate counterions. The conjugation in these systems despite presence of substituents is attributed to strong electrostatic interactions between the pyridinium ring substituents and the counter ions, which predominates over steric factors that are responsible for twisted backbones(5,6) in uncharged systems.

The polymerization reaction involves activation of the acetylenic triple bond in ethynylpyridines by different methods such as quaternization via a Menshutkin reaction (3,4), formation of donor-acceptor complexes with bromine (5) and by protonation by a strong acid (6). All methods result in transient activated species that undergo spontaneous polymerization, and are limited by relatively low molecular masses (~4000) for the product polymers. This may be attributed to a relatively slow activation step (which results in low concentration of the activated species) compared to rapid propagation and termination steps. In view of this, an alternative method was sought for a more rapid activation of the monomer. Such methods involve use of a highly reactive quaternizing agent that enables the isolation of the activated ethynylpyridinium salt as a stable intermediate.

A new route for polymerization of the acetylenic bond in ethynylpyridines is described. Unlike previous methods wherein quaternization resulted in spontaneous polymerization of the acetylenic bond, the present method affords isolation of the activated monomeric species in the form of alkylpyridinium salts. Polymerization of the activated monomers when initiated with nucleophiles such as pyridine resulted in substituted, ionic polyacetylenes with extensively conjugated backbones. Scheme 1 shows the monomers and proposed structures for the polymers obtained by the present method.

Experimental:

Materials: 2-Ethynylpyridine and 2-(trimethylsilyl)ethynylpyridine were obtained from Farchan Laboratories and distilled under vacuum before use. Trifluoromethane sulfonate was obtained from Aldrich Chemical Company and was used without further purification. Pyridine and DMSO (Aldrich) were distilled before use. **Measurements:** Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrophotometer using KBr pellets. UV absorption spectra were obtained at 22° C in DMSO on a Cary 9420 visible-ultraviolet spectrophotometer. Dilute solution viscosity measurements were made in DMSO at 28°C using a Cannon-Ubbelohde dilution type viscometer.

N-Methylethynylpyridinium triflates I, II: Were synthesized by the method described by File et al. (7) by reacting the ethynylpyridine with an equimolar amount of trifluoromethanesulfonate in anhydrous dichloromethane. The pyridinium salt was purified by recrystallization.

General procedure for polymerization: The activated monomer (0.2g) was dissolved in anhydrous DMSO (5ml). This was added to a stirred solution of pyridine (0.002g) in 5ml of DMSO at 20°C. The reaction mixture was stirred for 24 hours and the solvent removed under reduced pressure to yield a dark solid. This was extracted with ether and dried to yield the polymer as a black powder.

Results and Discussion:

The polyacetylenes Ip and IIP obtained from the reaction of monomers I and II respectively with pyridines possess highly conjugated structures as is evident from their absorption spectra. Both polymers show absorption maxima above 600nm for the unsaturated carbon backbone in the UV visible spectrum. The conjugation lengths are substantially higher than those for the polyacetylenes obtained by previously reported methods. Table I shows a comparative list of the absorption maxima for ionic polyacetylenes obtained by us by various activation processes. The conjugation lengths based on theoretical calculations assume a *trans-transoid* conformation for the polymers (6,8). Molecular dynamics calculations on these systems indicate that this conformation is a stable one for such ionic structures (9). The absorption maxima for both polymers Ia and Ib are close to that for *trans*-polyacetylene (630nm) and are, by far, the highest reported for substituted polyacetylenes. The $\text{C}\equiv\text{C}-\text{H}$ and the $\text{C}\equiv\text{C}$ bands at 3290 and 2109 cm^{-1} respectively in the infrared spectrum of the starting monomer are replaced by a broad band at 3400 cm^{-1} (hydrogen bonded ring C-H) and a strong one at 1612 cm^{-1} (C=C). Figure 1 shows the infra red spectra of monomer I and polymer Ia.

The polymerization of the ethynylpyridinium triflate salts Ia and II is readily initiated by nucleophiles such as pyridine or triphenyl phosphine. A similar polymerization mechanism has been reported for the corresponding 4-vinylpyridinium triflate salts (7,10). Unlike previous methods the present polymerization involves a non spontaneous process wherein the activation step is separated from the nucleophile initiated polymerization. A possible factor in the termination step due to presence of the excess quaternizing agent is thus avoided. The molecular masses of the resulting polymers are, however, slightly higher than those obtained by spontaneous polymerization processes. Optimization of reaction conditions for improvement of molecular masses in these systems is under investigation.

Conclusion:

The presently described polymerization reaction of ethynylpyridinium triflates initiated by nucleophiles offers a new route for the synthesis of highly conjugated, substituted polyacetylenes. Unlike the spontaneous processes described previously for the synthesis of such systems, the present method involves isolation of the activated pyridinium salt and a polymerization reaction that is non spontaneous. The resulting polymers have greater conjugation lengths and higher molecular masses than the former methods. Optimization of reaction conditions for improving molecular mass is currently in progress.

Acknowledgement:

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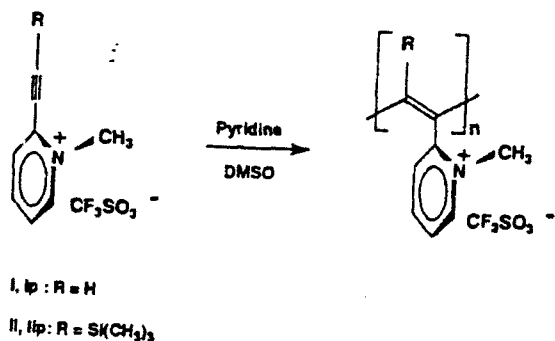
Table 1. Absorption maxima and conjugation lengths (n) of ionic polyacetylenes synthesized by different methods

Method	λ_{\max} (C=C) ^a (nm)	n^b (calc.)	$(\eta)_{inh}^c$ dL/g	Ref.
Menschutkin reaction	440-490	4-10	0.2	3,4
Halogen complex	450	8	0.1	5
Protonation	530	15	0.2	6
Triflate salt	610	22	0.3	this work

^a From UV-vis. spectra in DMSO at 22°C

^b From Lewis Calvin equation (Ref. 8)

^c In absolute methanol and DMSO at 28°C



Scheme 1

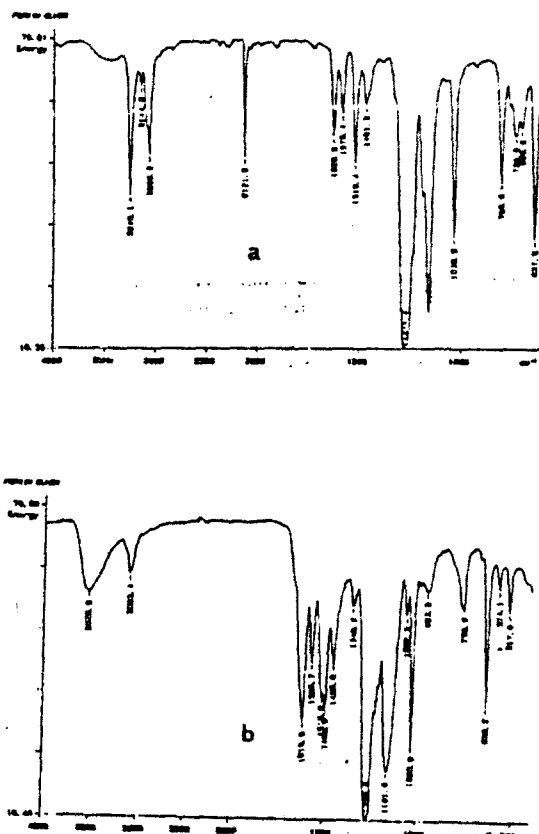


Figure 2: IR spectra of (a) monomer I and (b) polymer Ip

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Technical Report No. 5

**Ionic Polyacetylenes with Conjugated Backbones:
Kinetic Investigation of the Polymerization of 2-Ethynylpyridinium
Triflate**

by

L. Balough and A. Blumstein

ACS Polymer Preprints, vol. 34, 2, (1993)

University of Massachusetts Lowell
Department of Chemistry
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May 6, 1993

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<p>Polymerization of ethynylpyridines with nucleophiles results in substituted ionic polyacetylenes. The structural features of these polymers are unique with respect to their ionic nature, high degree of substitution and extensive backbone conjugation. Kinetic and mechanistic investigations were carried out on the title compound using pyridine initiator in methanol or pyridine as solvent at room temperature. In pyridine the reaction gave polymer while in methanol it led mainly to dimers. The reaction was monitored by IR and UV-visible spectra and the structure of the products were confirmed by NMR methods. The reaction was first order with respect to both the initiator and the monomer. Evidence is given for an anionic mechanism.</p>					
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IONIC POLYACETYLENES WITH CONJUGATED BACKBONES: KINETIC INVESTIGATION OF THE
POLYMERIZATION OF 2-ETHYNYLPYRIDINIUM TRIFLATE. L. Balogh and Alexandre Blumstein,
Department of Chemistry, Polymer Program, University of Massachusetts Lowell, Lowell,
Massachusetts 01854.

Polymerization of ethynylpyridines with nucleophiles results in substituted ionic polyacetylenes. The structural features of these polymers are unique with respect to their ionic nature, high degree of substitution and extensive backbone conjugation. Kinetic and mechanistic investigations were carried out on the title compound using pyridine initiator in methanol or pyridine as solvent at room temperature. In pyridine the reaction gave polymer while in methanol it led mainly to dimers. The reaction was monitored by IR and UV-visible spectra and the structure of the products were confirmed by NMR methods. The reaction was first order with respect to both the initiator and the monomer. Evidence is given for an anionic mechanism.

Ionic polyacetylenes with conjugated backbones: kinetic investigation of the polymerization of 2-Ethynylpyridinium methyl triflate.

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Introduction:

We have recently reported the synthesis of a new class of mono- and disubstituted ionic polyacetylenes with extensively conjugated backbones [1-7]. These polymers contain pyridinium ring substituents associated with halide, methanesulfonate or trifluoromethanesulfonate counterions. The structural features of these polymers are unique with respect to their ionic nature, high degree of substitution and extensive backbone conjugation.

These polymerization reactions involved a salt formation between the pyridine ring and the counterions formed from the quaternizing agents /or strong acids. The use of a highly reactive quaternizing agent such as methyl trifluoromethanesulfonate enabled us to isolate the real monomer, i.e., the ethynylpyridinium salt. Polymerization of this monomer when initiated with nucleophiles such as pyridine resulted in substituted ionic polyacetylenes. A chain-polymerization anionic mechanism was proposed for the formation of these ionic polyacetylenes [8] based on analogy with vinylpyridine.

Experimental:

2-Ethynylpyridine obtained from Lancaster Synth. Inc. was distilled under vacuum in nitrogen atmosphere before use. Pyridine (anhydrous) and methyl trifluoromethanesulfonate was purchased from Aldrich and were used as received. Methylenechloride was distilled from P_2O_5 twice. Other common solvents were distilled before use.

IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer between CaF_2 plates. UV-visible spectra were obtained on an IBM 9420 spectrophotometer at room temperature. NMR measurements were carried out by a Bruker-270 SY multinuclear spectrometer.

Synthesis:

N-Methylethynylpyridinium triflate (I) was synthesized in a MBraun 150M stainless steel glove box (Innovative Technology Inc.) under dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm) by reacting the 2-ethynylpyridine with a slight excess of methyl trifluoromethanesulfonate in anhydrous methylenechloride at $-20^\circ C$. This stable salt was used in the kinetic investigations after washing and drying.

Polymerization:

The monomer salt was dissolved in 5 ml of solvent at room temperature ($23^\circ C$) and the calculated amount of nucleophile was added by microsyringe during vigorous stirring on a Vortex mixer. A sample was measured into a Perkin Elmer FT-IR circular demountable cell (0.5 mm) and the disappearance of the $C\equiv C$ bond was monitored in the successive spectra.

In addition UV-visible spectra were also taken between 200 and 900 nm in order to follow the reaction.

For polymerization in pyridine a three-neck flask equipped with stirrer and condenser was used. The thoroughly ground solid triflate salt (54 mmol, 14.45 g) was added into 100 ml anhydrous pyridine under vigorous stirring. After 30 mins the solvent was evaporated on rotavap and the resulting black material was dissolved in 40 ml of methanol and then precipitated by 160 ml diethylether. This procedure was repeated three times to remove the low molecular weight oligomers. Finally the product was washed with diethylether and dried under reduced pressure at 40 °C to yield the polymer as a black solid (yield = 96 %).

Results and discussion:

Polymerization in pyridine:

Polymerization reactions in acetonitrile or DMF initiated with pyridine did not result in 100% conversion even in four days at room temperature, but after a rapid polymerization slowed down and finally stopped at incomplete conversions. However, when the reaction was carried out in anhydrous pyridine, i.e., in the solution of the initiator itself, instead of oligomers polymer was formed in an exothermic reaction. The average degree of polymerization was measured by ^{14}N NMR and was found equal to sixteen. The polymerization was completed within minutes revealing the fact that the rate of initiation is much lower than the rate of propagation and therefore the initiation is the rate determining step.

Oligomerization in methanol:

Pyridine initiator and methanol solvent were used to clarify the nature and kinetics of the oligomerization. The triflate salt dissolved in methanol proved to be a stable solution (oligomerization was less than 1 % in one week at room temperature). Methanol, being a polar protic solvent dissolves the reactants well and terminates the growing chains leading to dimers and low molecular weight oligomers. These oligomers display sharp NMR signals in contrast to polymers which ^1H and ^{13}C spectra show complicated overlapping patterns. However, the initiation step itself is not influenced by the protic nature of the solvent and does solely depend on the concentration and activity of nucleophiles present in the system.

The reaction between (I) and pyridine in methanol shows a linear $\ln[M_0/M]$ versus time function in the first stage, i.e., an apparent first order dependence with respect to the monomer concentration (Figure 1). (In the second stage of the oligomerization this function becomes curved possibly as a result of the chain transfer to the solvent.)

Varying the concentration of the initiator the kinetic order for pyridine is also 1.0 (Figure 2). The nucleophile-monomer adduct (II) reacts rapidly with the monomer to give oligomers. Due to a rapid proton-transfer the products are mainly dimers (III) and low molecular mass oligomers (Scheme 1). The structure of dimer(III) was confirmed by ^1H , ^{13}C and ^{14}N NMR.

Increase of the monomer concentration led to decreasing reaction rate in similarity to the ionic nucleophilic substitutions where only the dissociated ions are reactive.

Conclusions:

The kinetics of the polymerization of N-Methyl-2-ethynylpyridinium triflate initiated by pyridine was investigated in methanol and pyridine at room temperature. The oligomerization in methanol enabled us to separate the dimer and determine its structure with ^1H , ^{13}C and ^{14}N NMR. The mechanism displays the characteristics of an anionic polymerization. The reaction is first order both with respect to the initiator and the monomer. Dissolving the triflate salt in pyridine results in fast formation of the polymer indicating that the rate of propagation is much higher than the rate of initiation therefore the latter is the rate determining step. The exact nature of termination is under investigation.

Acknowledgment:

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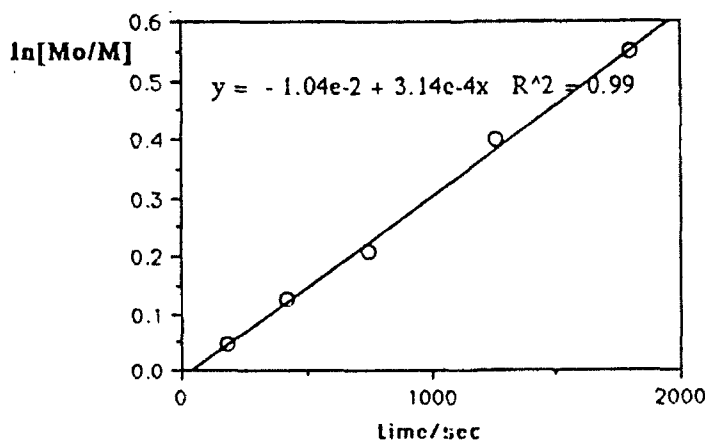


Figure 1.: Reaction of N-Methylethynylpyridinium triflate with pyridine in methanol at room temperature. $[\text{M}]_0 = 0.10 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 8.22$. Only the low conversion range is plotted.

(conv. < 0.42).

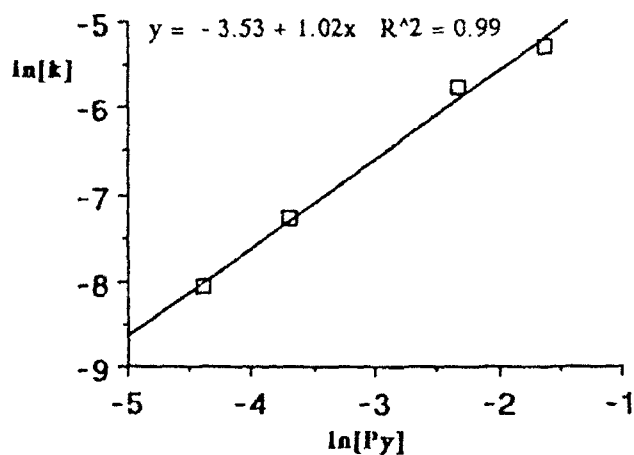
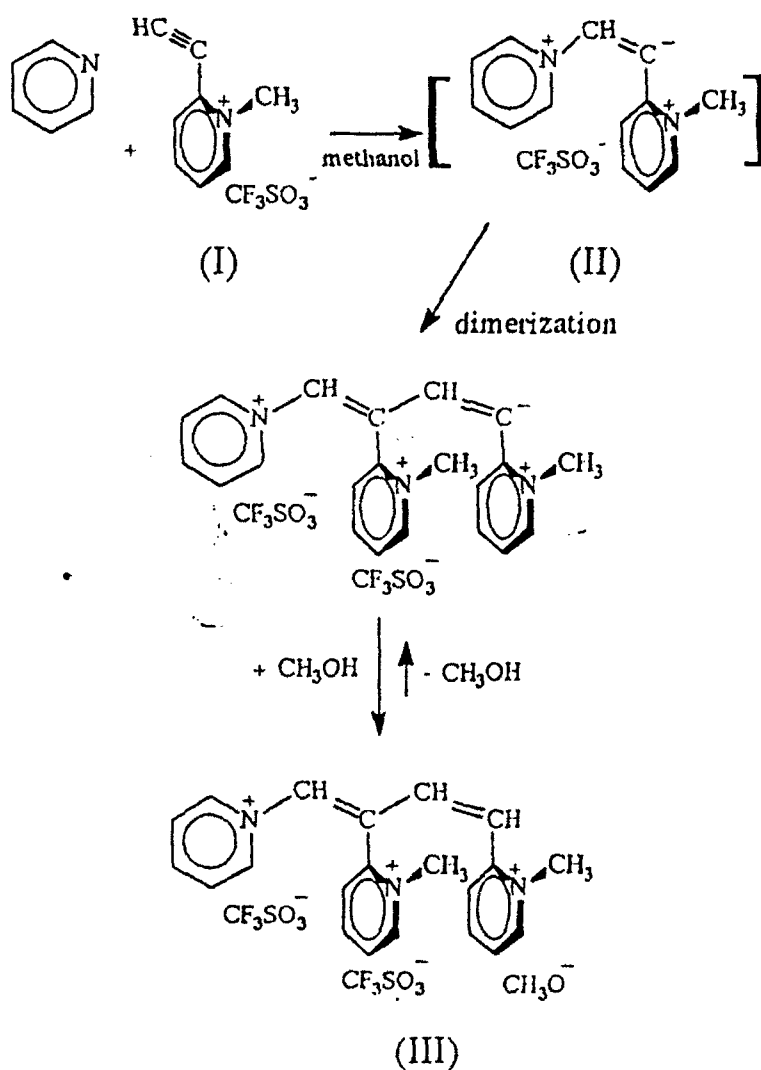


Figure 3.: Determination of the reaction order for pyridine in the oligomerization process.



Scheme 1.: Oligomerization in methanol initiated with pyridine.

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PART II

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d) Study of the family of novel polyacetylenes discovered in our laboratory in 1990 : extensively conjugated substituted ionic polyacetylenes. These novel polyacetylenes are soluble and stable up to 200 °C in air. They display conductivities when doped with iodine or TTF of up to $5 \cdot 10^{-2}$ S/cm. We found the acetylenic triple bond sufficiently activated by quaternization to undergo polymerization with a number of different initiators not only anionic but free radical. These polymers are being studied with respect to their conformation (modelling), their bulk properties (conductivity, optical properties such as NLO properties, film forming properties and last but not least the kinetics of polymerization which we hope will allow us to understand the mechanism(s) of formation of these rather unusual systems and to maximize their DP and their conjugation length which at present does not exceed 15-20.

e) The ONR support 1992-1993 allowed us to separate the two initiation reactions: the quaternization of the ethynyl pyridine (leading to the preparation of the monomer) and the initiation of the separated and quaternized monomer with a nucleophilic or a free radical initiator. This in turn paved the way to make a serious attempt at the understanding of the kinetic mechanism.

In addition to the study of kinetics we have discovered a solvatochromic effect prevalent in the radically prepared polyacetylene. This effect is explained hypothesizing a structural difference between the anionically prepared polymer and the free radically prepared one. It is to be pointed out that the unique feature of these polyacetylenic bearing a moiety susceptible to charge transfer conjugated to a conjugated sequence of double bonds in the backbone may allow for solvatochromic effects hitherto unknown for poly(monoacetylenes).

Finally, the ONR support allowed us to contribute to the modelling of such novel structures with the interesting result that extensive substitution of the triple bond does not preclude long conjugation in the polymer which is stabilized by the ionic framework.

f) We expect to understand better the mechanism(s) leading to formation of substituted ionic poly(acetylenes) and to maximize the DP and the conjugation length and improve the overall bulk properties of these ionomers through the continuation of the kinetic study.

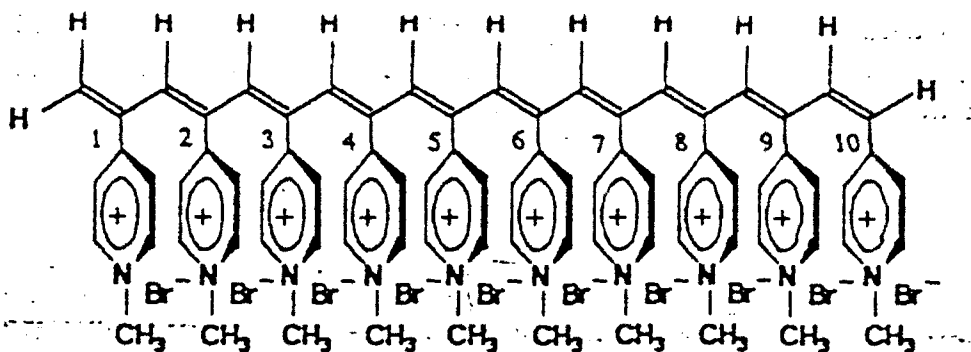
We expect also to study the potential applications of these polymers in the area of NLO, in the field of electroactive films. Of interest is also the study of composites of these polymers with halogenated ionomeric matrices (such as nafions for example) to explore the potential of these systems as membranes in separation techniques involving aqueous media.

These studies are of course contingent on continuous support of this project.

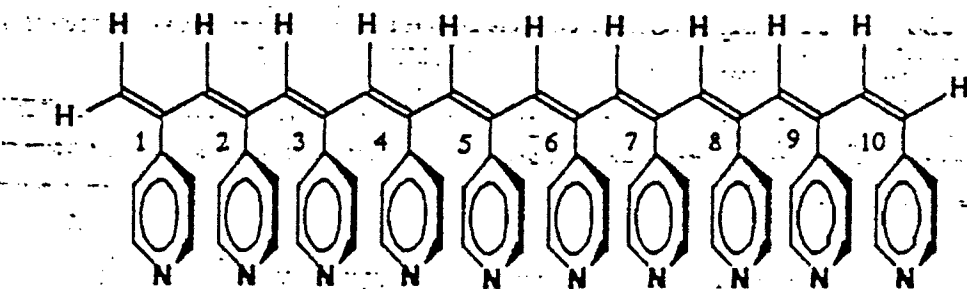
g) Dr. Lajos Balogh, Research Associate and Visiting Scholar.. Mr. C. Feng (grad. student)

PART III

A.

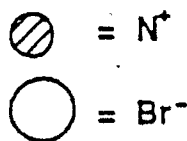
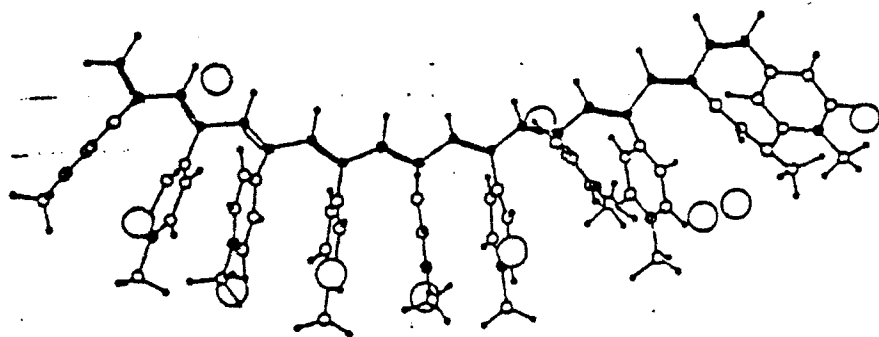


a

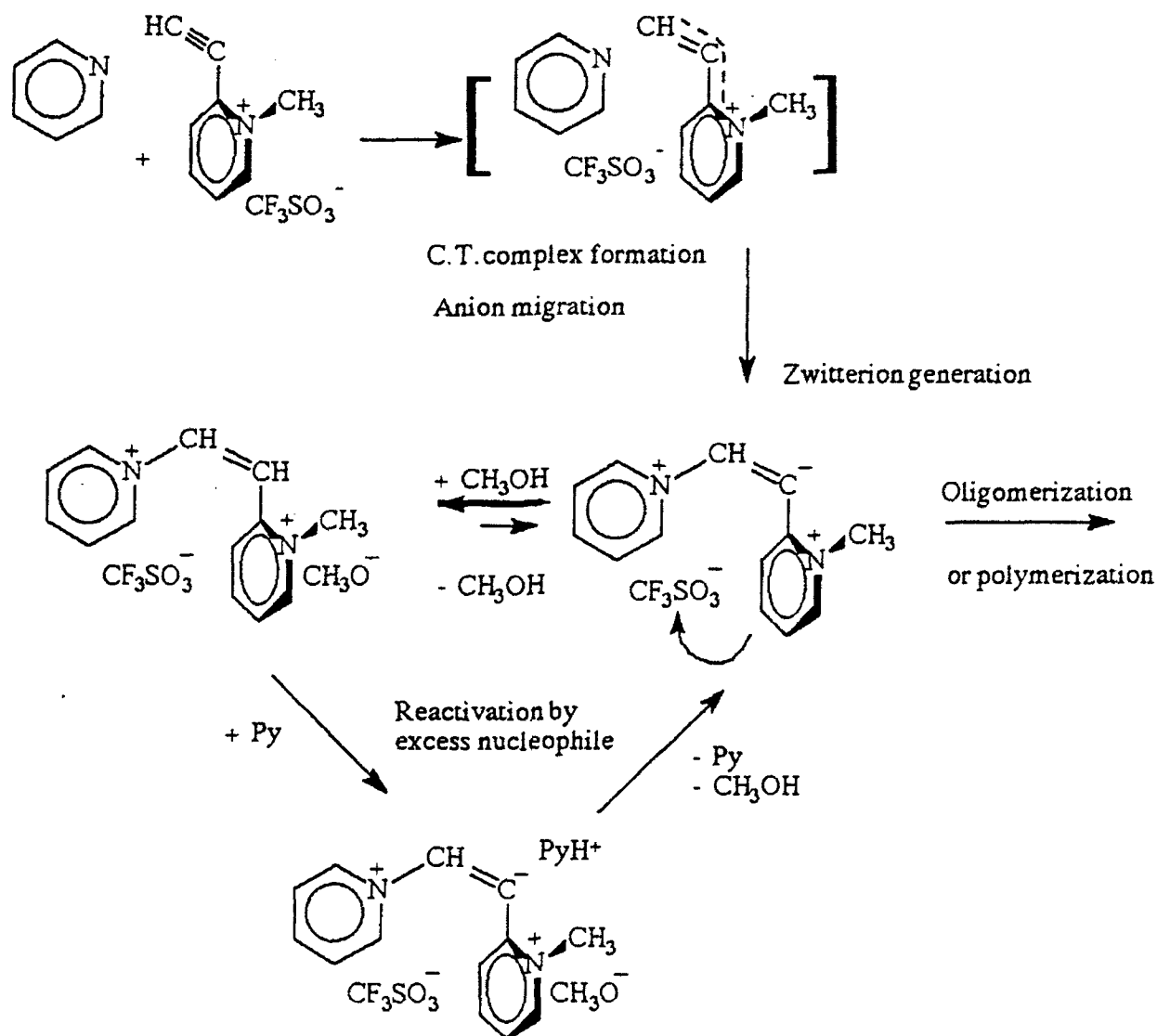


b

Substituted polyacetylene with 10 repeat units in the (a) charged and (b) uncharged states.

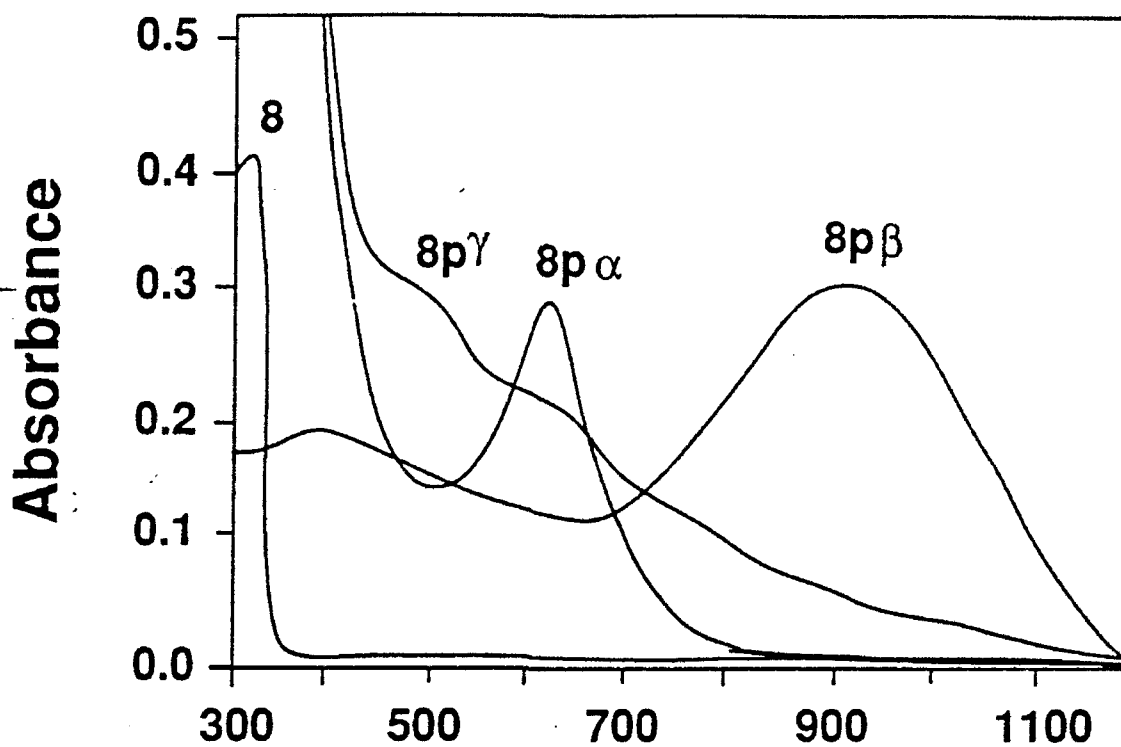


The most probable chain conformation (trans-transoid) of the ionic substituted poly(4-ethynylpyridiniummethyl bromide)

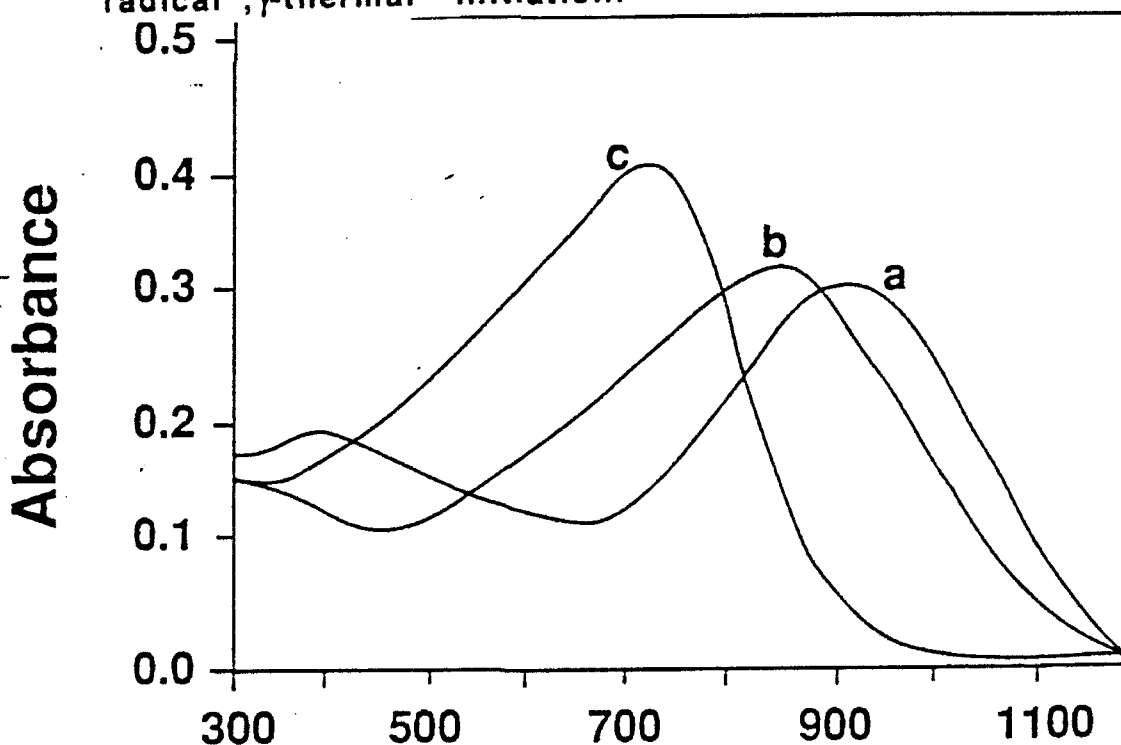


The initiation and propagation steps of the polymerization of 2-ethynylpyridinium triflate by a nucleophile(pyridine) in a protic solvent (methanol).

C



UV-VIS/NIR Spectra of poly(2-ethynylpyridiniummethyl triflates) in acetonitrile (10-6 g/L): α-nucleophilic; β-free radical; γ-thermal initiation.



Wavelength (nm)

Solvatochromic Effect of the free radically prepared poly(acetylene): UV-VIS/NIR Spectra of the β- poly(2-ethynylpyridiniummethyl triflates) in acetonitrile (10-6 g/L): a-after 0 min.; b-after 120 min.(equil.); c-in water (equil.).

✓

D This year the effort was concentrated on increasing the DP of ionic substituted polyacetylenes. This necessitates some understanding of the kinetic mechanism of the polymerization reaction which appears to be complex and to defy a standard classification.

We have succeeded in separating the overlapping quaternization and polymerization reactions which inhibited the study of the initiation and propagation steps. This was achieved by using a very fast quaternization agent- methyl triflate. It led to the isolation of the pure monomer the 2-ethynylpyridiniummethyl triflate. We have thus been able to study the mechanism of polymerization and to follow the kinetics of polymerization through the oligomerization into the polymerization stage. In addition, new solvatochromic phenomena were observed with oligomeric structures produced by free radical opening of the triple bond which appears to be sensitive not only to ionic but also to free radical initiation. The extensive conjugation of the backbone and of the charge bearing substituent appear to have important implications in charge transfer phenomena occurring within these novel polymer structures.